



**US Army Corps
of Engineers®**
Engineer Research and
Development Center

Sediment Capping and Natural Recovery

Contaminant Transport Fundamentals with Applications to Sediment Caps

David M. Petrovski, Maureen K. Corcoran,
James H. May, and David M. Patrick

September 2005

Sediment Capping and Natural Recovery

Contaminant Transport Fundamentals with Applications to Sediment Caps

David M. Petrovski

*Region 5
U.S. Environmental Protection Agency
77 W. Jackson Boulevard
Chicago, IL 60604-3511*

Maureen K. Corcoran and James H. May

*Geotechnical and Structures Laboratory
U.S. Army Engineer Research and Development Center
3909 Halls Ferry Road
Vicksburg, MS 39180-6199*

David M. Patrick

*The University of Southern Mississippi
118 College Drive
Hattiesburg, MS 39406-0001*

Final report

Approved for public release; distribution is unlimited

Prepared for U.S. Environmental Protection Agency
 Great Lakes National Program Office
 Chicago, IL 60604-3511

and U.S. Army Corps of Engineers
 Washington, DC 20314-1000

ABSTRACT: Engineered sediment caps and natural recovery are in situ remedial alternatives for contaminated sediments, which consist of the artificial or natural placement of a layer of material over a sediment deposit, respectively. In addition to physical isolation and the prevention of sediment erosion, the objective of these approaches includes mitigating the loss of dissolved contaminants from the sediment deposit to the overlying surface water. Whether engineered or placed naturally through sedimentation, migration of contaminants through the cover layer needs to be evaluated to forecast performance and compare the effectiveness of capping or natural recovery to other remedial options such as dredging. This report reviews the techniques commonly used to predict the migration of contaminants through sediment cover layers and to assess performance. Predicted upon the planar nature of the sediment deposit and cover layer, these techniques commonly take the form of vertically oriented one-dimensional (1-D) methods and models. These 1-D approaches use input values describing the characteristics of the sediment cap and the hydrogeologic surroundings and generate output values that are used to project cover-layer performance. The assumptions implicit in the use of the 1-D methods and models are also discussed. Much of the information in this report was gathered from standard references in the hydrogeologic literature.

DISCLAIMER: The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products. All product names and trademarks cited are the property of their respective owners. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Contents

Preface	vii
1—Introduction	1
2—Transport Mechanisms and Processes That Control Cap Performance	4
Groundwater/Surface-Water Interactions	4
Sediment Cap Geometry and One-Dimensional Transport Models	6
Contaminant Source Concentration (C_o)	9
Contaminant Transport Mechanisms	12
Molecular diffusion	13
Advection	20
Assumptions associated with advective transport equations	26
Mechanical mixing	27
Hydrodynamic dispersion	30
Contaminant breakthrough and spatial distribution curves	33
Contaminant transport: advection versus diffusion	33
Overview of Contaminant Sorption	37
Hydrophobic organic contaminants	41
Metal contaminants	43
Contaminant Flux Equations	44
3—Transport Models and Cap Performance Predictions	47
Overview	47
One-Dimensional Transport Models and Sediment Caps	49
The Diffusion Transport Model	50
Boundary and initial conditions	52
Solutions applicable to sediment caps	53
Solution interpretation	54
The Advection Transport Model	56
Initial condition	58
Solutions applicable to sediment caps	59
Solution interpretation	59
The Advection-Dispersion Model	60
Boundary and initial conditions	62
Solutions applicable to sediment caps	62
Solution interpretation	64
Significance of hydrodynamic dispersion	66
Cap Predictions Versus Cap Performance	67

4—Conclusions.....	69
References	71
SF 298	

List of Figures

Figure 1.	Groundwater/Surface-Water Interactions: The solid curves represent groundwater flow lines, while the dashed curves represent positions of equal energy or hydraulic head. The flow lines have a downward tilt in the uplands, which are referred to as groundwater recharge areas. Flow lines have an upward tilt in the lowlands called groundwater discharge areas. Note: vertical exaggeration has enhanced the curvature of the flow and equipotential lines (from Hubbert 1940)	4
Figure 2.	Conceptual Model: The conceptual model for this report consists of a contaminated-sediment layer and an overlying cover layer or sediment cap of thickness \mathcal{L} . Both layers are uniform in thickness and horizontal in orientation. A vertically oriented 1-D coordinate system is used to predict contaminant migration through the cap. The sediment layer is underlain by <i>in situ</i> uncontaminated geologic materials.....	7
Figure 3.	Contaminant Phases: C_s represents contaminants sorbed to the sediment solids and C_o , the dissolved contaminant concentration at equilibrium. The figure also depicts the grain-size variation typically associated with naturally deposited sediment and the more uniformly sized materials associated with an engineered cap.....	8
Figure 4.	Contaminant Migration: Contaminant migration from a uniform source through a horizontal homogeneous cap will occur as horizontal planes of equal concentrations, which can be tracked with a vertically oriented coordinate system. The shading in the sediment cap represents the presence of dissolved contaminants. As the contaminants are migrating upward from the sediment layer, the darker shading at the base of the cap depicts higher contaminant concentrations	10
Figure 5.	Diffusion: The results of diffusion as seen through the spread of a drop of ink in a beaker of motionless water. The t_0 represents the initial distribution of ink, while t_1 and t_2 represent the distribution at later times	13

Figure 6.	Gaussian Representation of a Diffusing Ink Drop: The initial width of the drop is $2a$, extending from $x-a$ to $x+a$. At any time t after the start of diffusion, the distribution of ink can be represented by a Gaussian or normal curve (from Fetter 1999)	14
Figure 7.	Sigmoidal Contaminant Distribution Along the Contaminant Front: Relationship between the Gaussian and sigmoidal distribution along the contaminant front is indicated in Figures 7(a) and 7(b) for time t_2 . Figure 7(a) depicts the contaminant front where the direction of interest is horizontal, while Figure 7(b) shows a similar depiction where the direction of interest is oriented vertically. Figures 7(c), 7(d), and 7(e) show the contaminant front at times t_0 , t_1 , and t_2 . At t_0 , the contaminant front is at the base of the cap, while t_1 and t_2 show the migration and lengthening of the contaminant front. All concentrations are normalized to the source concentration (C/C_o).....	15
Figure 8.	Components of Hydraulic Head in a Piezometer: Hydraulic head is a measure of the energy per unit weight at a point and has two components: elevation head (z) and pressure head ($P/(\rho g)$) (from Freeze and Cherry 1979).....	21
Figure 9.	General Flow Lines and Equipotential Lines in Temperate Groundwater Discharge Areas: Groundwater motion at any point along a flow line (shown in red) can be depicted as a vector. The vector can be separated into horizontal and vertical component vectors. The upward vector component of the flow line is v_z . The vector's magnitude reflects the flux. Locations associated with equal hydraulic head values (equipotential lines) are depicted in blue. Note: vertical exaggeration enhances the appearance of V_v	22
Figure 10.	Causes of Mechanical Microdispersion: Pore-scale velocity variations that result in mechanical dispersion in the direction of flow (from Fetter 1999)	28
Figure 11.	Hydrodynamic Dispersion: Hydrodynamic dispersion reflects the combined influences of diffusion and mechanical mixing (after Freeze and Cherry 1979).....	31
Figure 12.	Contaminant Breakthrough and Distance Curves: Figure 12a depicts the concentration increase observed at a given point (z) in the cap through time while 12b depicts the concentration distribution along the contaminant front at different points in time (t_0 , t_1 , t_2 , t_3). The “dot” represents the center of the contaminant front (where C/C_o equals 0.5), which travels at v_z . The distance of transport (z) equals the product of v_z and the time of transport (t). Figure 12c is a cross section showing the migration and lengthening of the contaminant front through the cap with time (after Freeze and Cherry 1979).....	34

Figure 13.	Advective Transport: Ignoring mechanical dispersion, the contaminant front will move vertically upward through the cap as a horizontal plane at velocity v_v , assumed to be a constant. As the cap thickness (L) is a constant, the breakthrough time (T_B) equals L/v_v (after Freeze and Cherry 1979)	35
Figure 14.	Contaminant Fronts for Retarded Versus Nonretarded Contaminants: Sorbing contaminants have lower rates of advection and hydrodynamic dispersion and, therefore, narrower fronts, which lag behind nonretarded contaminants at any transport time t (after Freeze and Cherry 1979).....	40
Figure 15.	Contaminant Flux Into and Out of an REV: For a vertically oriented 1-D analysis, transport in the x (F_{cx}) and y (F_{cy}) directions is ignored. F_{cz} represents the vertical contaminant flux and depends upon the process being represented. For diffusion, $F_{cz} = -D_{ez}n_e dC/dz$ (Equation 9). For advection, $F_{cz} = v_z n_e C_o$ (Equation 18). For advection and hydrodynamic dispersion, $F_{cz} = v_z n_e C - D_{Lz} n_e dC/dz$ (Equation 43). As this report considers 1-D transport only, F_{cz} is represented as F_c (from Freeze and Cherry 1979)	53
Figure 16.	Solution to the Diffusion Transport Model: Starting at time t_0 , the contaminant front will move upward into the cap and moderate into an interval. At times t_1 and t_2 , the contaminant front is well below the top of the cap at L and the arguments of the $erfc$ in Equations 51 and 53 are large, resulting in a C/C_o ratio of approximately zero. At t_3 , the argument of $erfc$ and the C/C_o ratio are approximately 0.5	57
Figure 17.	Solution to the Advection-Dispersion Equation: Starting at t_0 , the contaminant front will move into the cap and moderate into an interval. At t_1 , the argument of the $erfc$ in Equations 66 and 67 is large ($RL > v_v t$ and $L > v_v t$), the C/C_o ratio is approximately zero, and the contaminant front is well below the top of the cap. At t_2 , the argument of the error function is zero ($RL = v_v t$ or $L = v_v t$), C/C_o equals 0.5, and the contaminant front has reached the top of the cap. At t_3 , the argument of the $erfc$ is negative ($RL < v_v t$ or $L < v_v t$), C/C_o equals one, and the contaminant front has passed through the cap	65

Preface

This report was prepared by Mr. David M. Petrovski of the U.S. Environmental Protection Agency (USEPA), Region 5; Ms. Maureen K. Corcoran and Dr. James H. May of the U.S. Army Engineer Research and Development Center (ERDC), Geotechnical and Structures Laboratory (GSL); and Dr. David M. Patrick of The University of Southern Mississippi.

The research project was funded by the USEPA Great Lakes National Program Office, Dr. Marc Tuchman, Program Manager, and by the U.S. Army Corps of Engineers' Dredging Operations and Engineering Research Program, managed by the ERDC Environmental Laboratory (EL), Dr. Michael Palermo, Program Manager. The contributions of Dr. Charles Dunning and Mr. Daniel Feinstein, U.S. Geological Survey, to Chapter 2 of the report are gratefully acknowledged. Technical reviewers were Dr. Tommy Myers, ERDC EL; Dr. Danny Reible, University of Texas; and Dr. James Weaver, USEPA Office of Research and Development.

Permission to use copyrighted material was obtained from the publishers as follows: *The Journal of Geology*, 1940, University of Chicago Press (Figure 1); *Contaminant Hydrogeology*, Second Edition, 1999, Pearson Education, Inc. (Figures 6 and 10); and *Groundwater*, First Edition, 1979, Pearson Education, Inc. (Figures 8 and 15).

The work was conducted under the supervision of Dr. Lillian D. Wakeley, Chief, Engineering Geology and Geophysics Branch; Dr. Robert L. Hall, Chief, Geosciences and Structures Division; and Dr. David W. Pittman, Director, GSL.

COL James R. Rowan, EN, was Commander and Executive Director of ERDC, and Dr. James R. Houston was Director.

1 Introduction

Sediments reside at the interface of groundwater and surface-water regimes. For a variety of physical and geochemical reasons, sediments function as a sink for numerous contaminants released to surface water from both point and non-point sources. Once contaminated, the sediments can subsequently act as a source of contamination to surface water, groundwater, and biota.

An engineered cap is an *in situ* remedial option for contaminated sediments consisting of the placement of one or more layers of material over a sediment deposit (U.S. Environmental Protection Agency (USEPA) 1998), while “natural recovery” relies upon the ongoing process of physical sedimentation to cover the contaminated sediment deposit with a clean or cleaner layer of more recently deposited material (National Research Council 1997, 2001). The purpose of *in situ* capping or natural recovery is to physically isolate contaminated sediments, prevent suspension or resuspension and transport of contaminated sediments to downstream locations, and mitigate the dissolved contaminant flux from the sediment layer to the overlying surface water body.¹ Proper cap placement or favorable natural deposition should preclude direct contact by aquatic organisms with contaminated sediments and reduce the potential for suspension or resuspension. Contaminant flux mitigation occurs through sorption of contaminants to the matrix solids composing the cover and extension of the time needed for the contaminants to migrate through the cover layer.

Whether placed naturally or artificially, the transport of contaminants through the cover needs to be predicted to assess cap performance and project impacts to surface-water quality and biota, and to compare the effectiveness of capping or natural recovery to other remedial options such as dredging. This report reviews methods commonly used to predict the transport of dissolved contaminants from a deposit of contaminated sediment through an overlying porous and permeable cover layer (the sediment cap). As discussed, these methods are subject to a variety of assumptions and limitations. Consequently, performance predictions produced by these methods need to be subsequently assessed by a monitoring program designed to measure the actual performance of the cap in the field.

Contaminant movement or migration is termed contaminant or mass transport. Contaminant transport through a sediment cover composed of porous and

¹ Contaminant flux is defined as the contaminant mass passing through a unit area per unit time.

permeable material can be caused by the presence of spatial gradients in the dissolved contaminant concentrations (diffusion) or the bulk flow of groundwater due to spatial energy gradients (advection). In many settings, contaminant transport through the sediment cover will be dominated by advection, which will in turn be dependent on the magnitude of the interactions and exchanges between ground and surface water at the site (Liu et al. 2001). For example, nearshore portions of lakes and streams in large temperate regions of the United States commonly act as groundwater discharge areas. Groundwater discharge areas are sites where water exits the groundwater flow system and enters the surface-water regime. In groundwater discharge areas, chemistry of the groundwater can be altered by passage through a layer of sediment associated with contaminants capable of partitioning to water. If the groundwater subsequently discharges to surface water, the entrained contaminants can also be released to the overlying surface-water body.¹ Consequently, a detailed evaluation and understanding of the hydrogeology at the sediment site is a critical factor for the evaluation of a capping or natural recovery proposal (Winter 2002). This site-specific information should be incorporated into the method and be reflected by the predictions used to forecast the performance of the sediment cover layer.

For most cap designs and natural recovery scenarios, the sediment cover layer consists of one or more layers of granular material tens to hundreds of meters in horizontal extent with a total thickness of a meter or less. Conceptually, the cover layer can be viewed as the addition of a thin horizontal layer of porous material to the boundary of the groundwater flow regime at the surface-water/sediment interface. Given similar hydraulic properties, groundwater velocities within both the sediment and cover layer can be assumed to be comparable. Therefore, the impact of the sediment-cover layer on the local groundwater flow field and the transport processes at the site should be minimal. Compliance with these assumptions will allow the characterization data collected at a proposed capping or natural recovery site and the projected properties of the cap to be used to predict the performance of the sediment cover using the methods provided in this report.

Assuming the sediment cover is physically stable over time, i.e., no erosion, cover performance can be defined in terms of the extent of contaminant containment provided by the cover layer. In this report, predictions regarding contaminant containment are provided by one-dimensional (1-D) contaminant transport methods and models. Vertically oriented through the cover layer, use of 1-D approaches rests upon the planar geometry and horizontal orientation of most sediment cover layers. Given these presumptions, a vertically aligned 1-D analysis would be associated with the shortest distance of separation between the underlying sediment layer and surface water, and would therefore be in the direction of greatest environmental significance for biota and surface-water quality. Commonly, 1-D analysis methods are used to predict the performance of two-dimensional (2-D) barrier systems such as slurry walls, landfill liners, and sediment covers (Rumer and Mitchell 1995; USEPA, Appendix B 1998).

¹ Alternately, in groundwater recharge areas, the quality of the groundwater beneath a deposit of contaminated sediment could be degraded by the passage of surface water through the sediment layer.

This report is divided into two sections. The first section (Chapter 2) provides a discussion of the mechanisms that participate in the transport of contaminants through a sediment cap. The second section (Chapter 3) discusses the performance of an engineered or natural-deposited sediment cap in the context of 1-D contaminant-transport models. Each of these models conceptually represents the mechanism(s) affecting transport and includes a governing equation mathematically defining transport parameter interactions and a solution to the governing equation reflecting initial and boundary conditions appropriate for sediment caps placed naturally or artificially.

2 Transport Mechanisms and Processes That Control Cap Performance

Groundwater/Surface-Water Interactions

Groundwater flow forms a portion of the hydrologic cycle. As implied by the name, the hydrologic cycle is the endless circulation of water between the oceans, atmosphere, and the continental areas of the planet. It can be considered a closed system with regard to water. In contrast, the hydrologic cycle is driven by the energy of the sun, and is an open system with regard to energy.

Input into the hydrologic cycle occurs in the form of precipitation. In a temperate terrestrial setting with relief, precipitation commonly results in a water table, which forms a subdued replica of the topographic highs and is coincident with the ground surface in the topographic lows (Freeze and Cherry 1979). Figure 1 is a simplified cross section on a regional scale of an unconfined aquifer

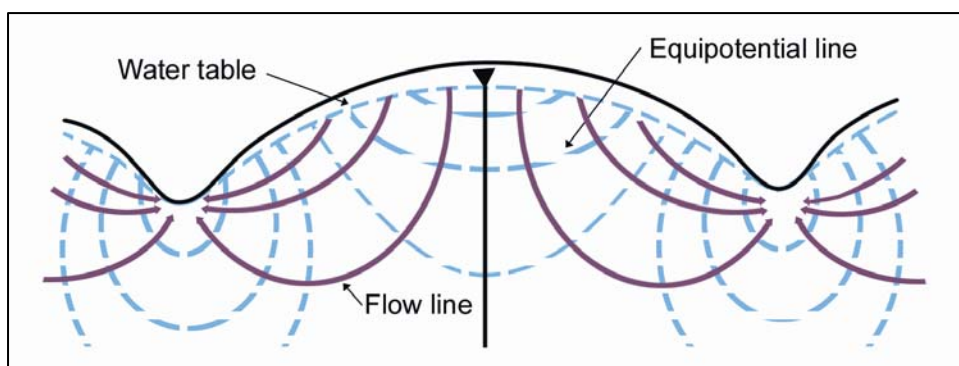


Figure 1. Groundwater/Surface-Water Interactions: The solid curves represent groundwater flow lines, while the dashed curves represent positions of equal energy or hydraulic head. The flow lines have a downward tilt in the uplands, which are referred to as groundwater recharge areas. Flow lines have an upward tilt in the lowlands called groundwater discharge areas. Note: vertical exaggeration has enhanced the curvature of the flow and equipotential lines (from Hubbert 1940)

underlain by a geologic layer with a notably lower ability to transmit water. The cross section is drawn perpendicular to a series of parallel ridges and valleys composed of geologic materials, which are homogenous and isotropic. The paths of groundwater flow are indicated by the solid red curves.

Groundwater flow can be described as a vector phenomenon, possessing both magnitude and direction. In Figure 1, flow lines are initiated in the topographic highs and progress until terminated in the topographic lows. The direction of groundwater flow at any point along the flow path is along the tangent to the flow line at that point. The solid lines of flow in red in the figure are drawn perpendicular to a set of dashed lines in blue. The dashed blue lines, referred to as equipotential lines, represent locations of equal energy or hydraulic head, a concept that will be discussed later. Groundwater motion is always from locations associated with high values of hydraulic head to locations associated with low values. Two-dimensional cross sections, such as Figure 1 depicting a set of lines of uniform energy and flow lines, constitute a flow net. As shown, in an isotropic medium, flow and equipotential lines intersect at right angles.

Uplands are termed groundwater recharge areas, and the lowlands are termed groundwater discharge areas. Recharge areas can be defined as those portions of the drainage basin in which the groundwater flow path has a downward component. In contrast, discharge areas can be defined as areas where the flow of groundwater has an upward component, and where water exits the groundwater regime and becomes surface water. Discharge areas commonly include the near-shore portions of lakes and rivers. As contaminated sediments frequently accumulate in the nearshore portions of surface water bodies, the upward component of groundwater flow in a discharge area can have significant implications for cap performance.

In an industrial setting, sediment accumulations at the interface between the ground- and surface-water regimes can be associated with a variety of contaminants that were originally released from point and nonpoint sources. In the presence of discharging groundwater, contaminants can be driven upward from the sediment layer to the overlying surface water.¹ In contrast, contaminated sediment located in an area where surface water is discharging to groundwater can result in impacts to groundwater quality.

The preceding descriptive conceptual model of regional steady-state groundwater flow in a homogenous, isotropic unconfined aquifer was first presented by M. K. Hubbert (Hubbert 1940) and is discussed in detail in most hydrogeologic textbooks (e.g., Freeze and Cherry 1979, Domenico and Schwartz 1990, Fetter 2001). For further information regarding ground- and surface-water interactions at potential capping and natural recovery sites, refer to Winter (2002).

¹ It should also be noted that the water quality of a surface-water body can also be affected by the discharge of groundwater from upland contaminant sources.

Sediment Cap Geometry and One-Dimensional Transport Models

The conceptual model used throughout this report consists of an accumulation of contaminated sediment deposited at the bottom of a river or lake (hereafter referred to as “the contaminated sediment layer” or “the sediment layer”) and an overlying porous and permeable sediment cover layer (hereafter referred to as “the sediment cap,” “the capping layer,” “the cap,” or “the cover layer”). The layer of contaminated sediment overlies *in situ* uncontaminated geologic materials (Figure 2). As the thickness of the contaminated sediment layer and cap are commonly measured in terms of meters or less, and their horizontal extent is measured in terms of tens or hundreds of meters, the sediment layer and the cap can be viewed as two-dimensional. That is, the contaminated sediment layer can be conceptualized to be a planar source of dissolved contaminants and the overlying cap as a planar barrier to contaminant migration. For simplicity, this conceptual model considers both the sediment layer and the cap to be horizontal in orientation and uniform in thickness. Furthermore, the sediment and the cap are assumed to be physically stable through time and therefore unaffected by physical processes such as erosion. Contaminants that pass through the cap are released to surface water and the ambient environment. Both the cap and the underlying sediment are considered to be porous, permeable, uniform in material properties, and saturated with water of uniform density and viscosity.

A 1-D coordinate system orientated vertically through the horizontal capping layer can predict the extent of contaminant containment provided by the cap. This approach is based upon the planar geometry associated with most sediment deposits and subaqueous caps. Aligned with a vertically oriented z -axis, the 1-D coordinate system has an origin at $z = 0$ coincident with the bottom of the cap (the top of the contaminated sediment layer) and extends vertically to $z = \mathcal{L}$, at the top of the cap. Consequently, the thickness of the cap is \mathcal{L} .¹ Such a vertically oriented contaminant transport model through the horizontal capping layer is aligned with the shortest distance between the sediment layer and surface water, and therefore in the direction of greatest environmental significance for biota and surface-water quality.

Though sediment contamination can occur in many forms, this report will address only contaminants in the sorbed and the dissolved phases. Aqueous phase contaminants will occur in the contaminated sediment layer as a result of partitioning between the contaminants sorbed to the matrix solids (C_s) and the water in the voids between the matrix solids (Figure 3). At equilibrium, this concentration is known as the source concentration (C_o). Because of the hydrophobic nature of most sediment contaminants, the contaminant mass in solution will almost invariably be significantly less than the contaminant mass associated with the sediment solids.

¹ The \mathcal{L} used in this report can be viewed as equivalent to the effective cap thickness (L_e) as defined by Reible (USEPA 1998, Appendix B). Effective cap thickness is the initial cap thickness minus the thickness affected by bioturbation, compaction, and the cap interval impacted by the short-term pore water migration due to sediment-layer compaction caused by cap placement.

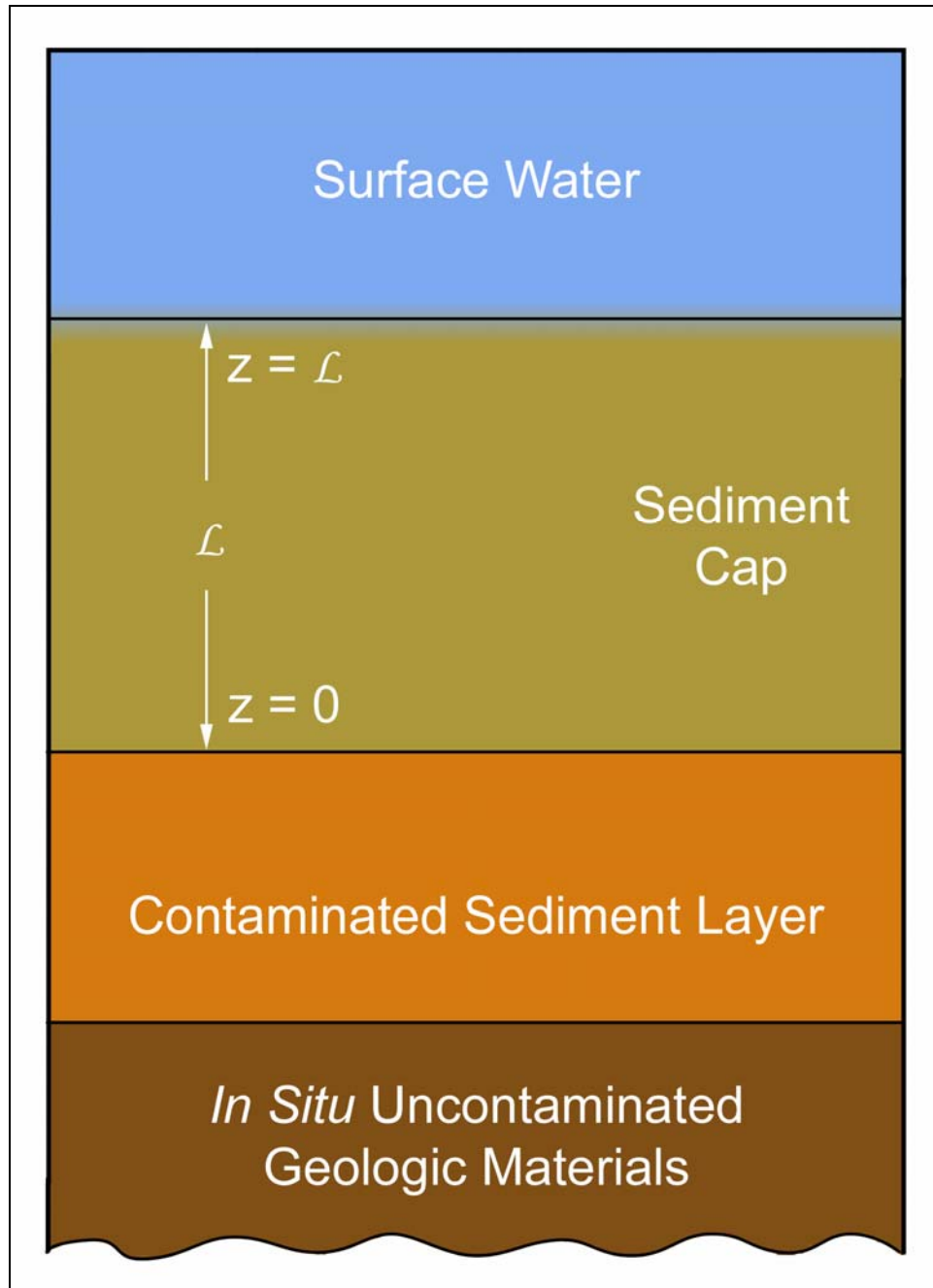


Figure 2. Conceptual Model: The conceptual model for this report consists of a contaminated-sediment layer and an overlying cover layer or sediment cap of thickness L . Both layers are uniform in thickness and horizontal in orientation. A vertically oriented 1-D coordinate system is used to predict contaminant migration through the cap. The sediment layer is underlain by *in situ* uncontaminated geologic materials

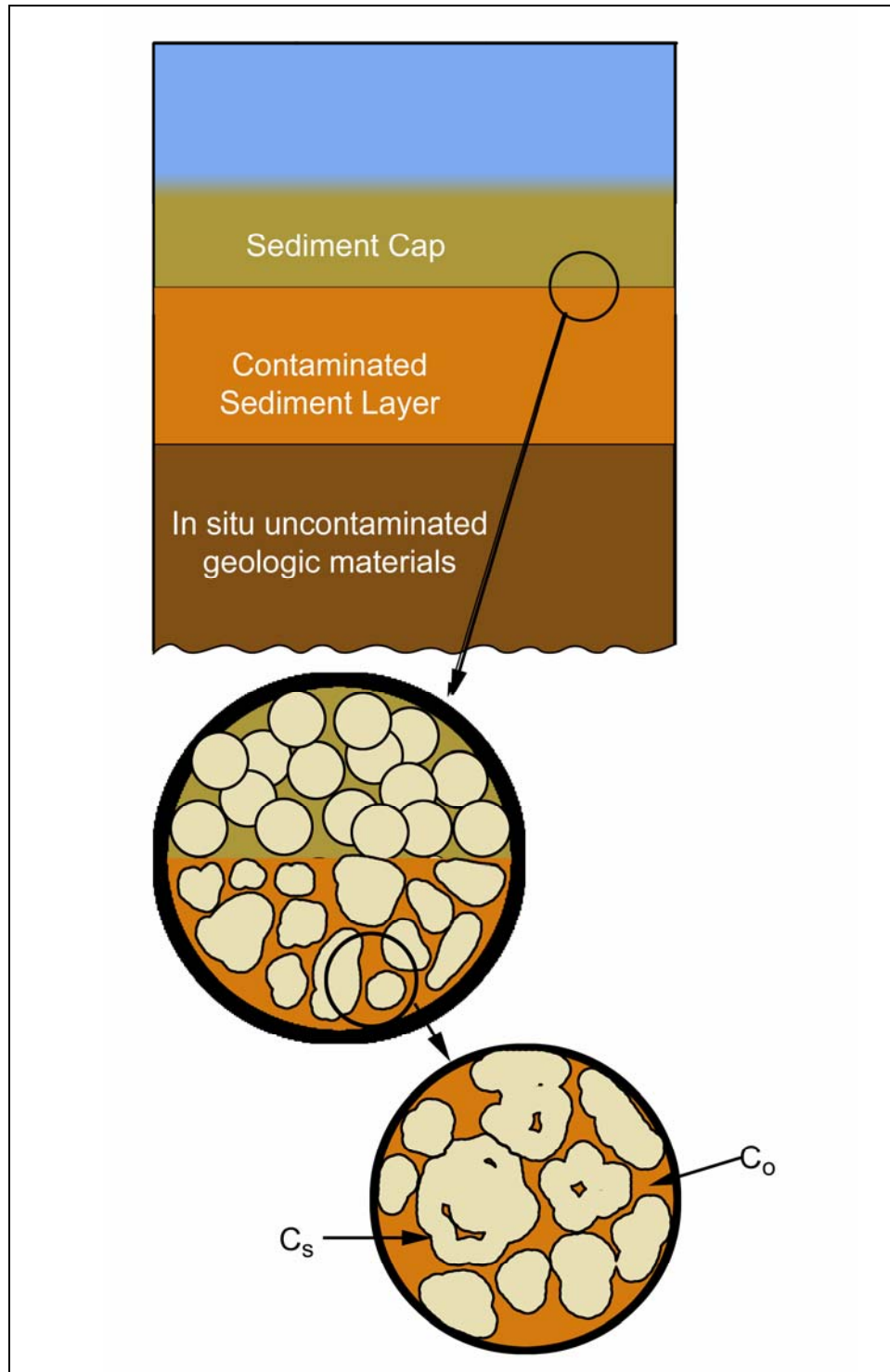


Figure 3. Contaminant Phases: C_s represents contaminants sorbed to the sediment solids and C_o , the dissolved contaminant concentration at equilibrium. The figure also depicts the grain-size variation typically associated with naturally deposited sediment and the more uniformly sized materials associated with an engineered cap

For this report, contaminant transport through the cap will occur only in the dissolved aqueous phase. The initial dissolved contaminant concentration within the cap will be presumed to be zero. Increases in the dissolved contaminant concentrations within the saturated pore space of the cap will be assumed to be the result of the transport of dissolved contaminants from the underlying sediment layer only. As transport moves a portion of the contaminant mass upward into the cap, a compensating contaminant mass sorbed to the sediment solids will dissolve so as to maintain the dissolved contaminant concentration in the sediment layer at the source concentration.

Conceptually, contaminant migration from a homogeneous source (the sediment layer) through a planar, horizontal, homogeneous sediment cap will occur as horizontal planes of equal contaminant concentrations (Figure 4). This will occur either in the absence of groundwater flow or in a setting associated with a uniform groundwater flow regime.¹ Consequently, monitoring devices placed randomly across the cap would simultaneously record the passage of the contaminants through the cap as the same sequence of events. The increase in contaminant concentrations measured by such a monitoring device and marking the passage of the contaminant through the cap would continue until the source concentration (C_o) was attained. Uniform thickness, a horizontal orientation, and spatial uniformity in the contaminant transport process are commonly implicitly assumed when 1-D models are used to predict cap performance.

In contrast to the sequence of events summarized above, for most capping situations in the field, spatial variations in the underlying sediment, the cap, and the surrounding materials preclude such uniformity. Therefore, real-world contaminant migration through the cap will not occur as horizontal planes of constant concentration, and monitoring devices placed at randomly selected locations on the surface of the cap will not simultaneously record the passage of the contaminant as the same series of events.

Contaminant Source Concentration (C_o)

In the field, the dissolved contaminant source concentration in the sediment layer can be reduced through a variety of mechanisms, which include contaminant decay, losses due to mass transport, or changes in geochemical conditions. For organic compounds, contaminant decay is caused by chemical or biological reactions and can occur in both the sorbed (C_s) and dissolved phases. In the absence of radioactive decay, the concentration of metals in the sediment layer available for transport can be reduced by changes in the valence or charge associated with the metal.² Changes in valence are due to alterations in the redox or the oxidation/ reduction characteristics and can result in precipitation, sorption, or the dissolution of a metallic contaminant. For both organic compounds and

¹ The process driving contaminant migration through the cap in the absence of groundwater flow is termed diffusion and is discussed later in the report.

² Valence or the valence number can be defined as the electrical charge atoms acquire when dissolved as ions in an aqueous solution (Faure 1998).

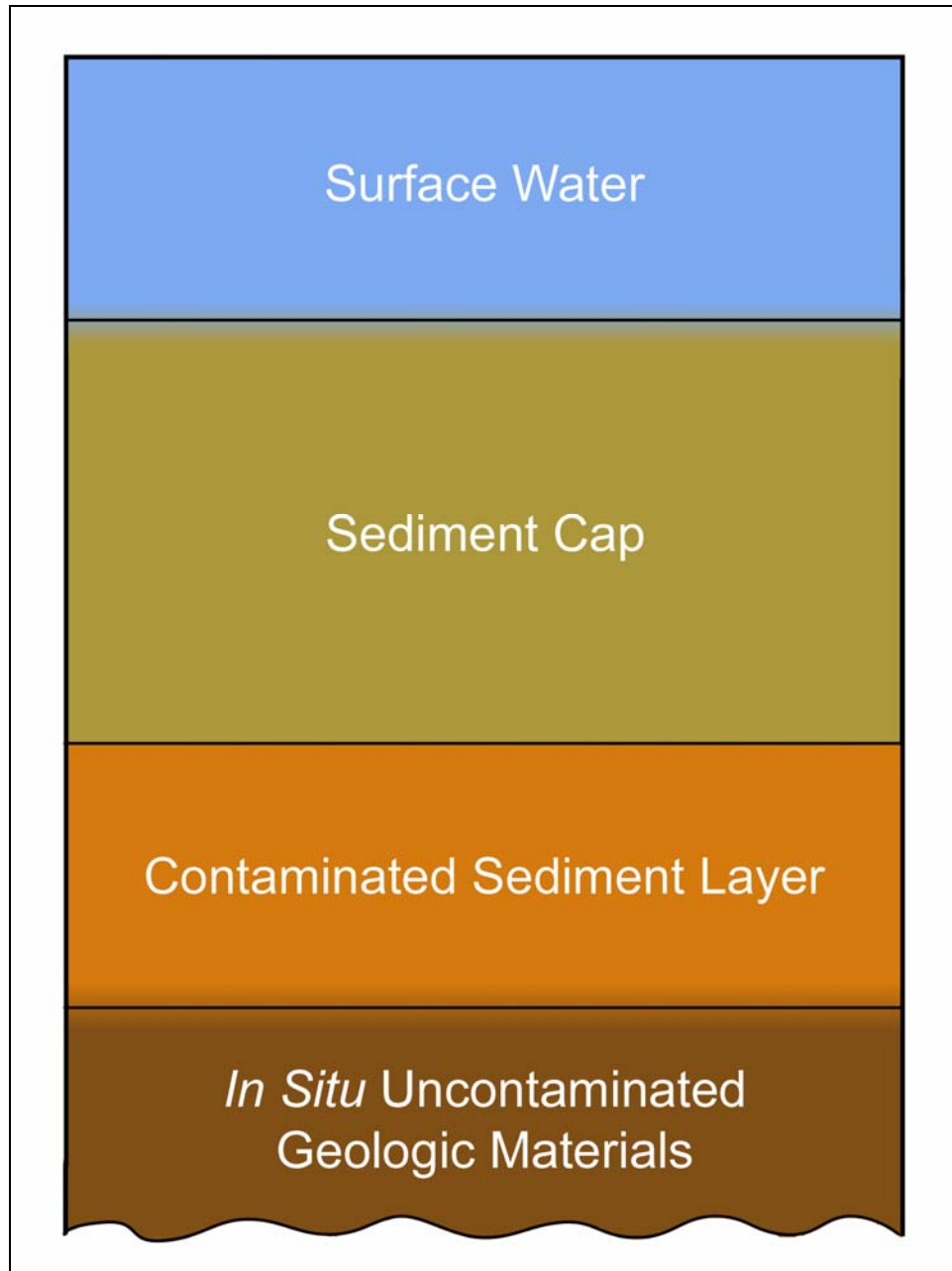


Figure 4. Contaminant Migration: Contaminant migration from a uniform source through a horizontal homogeneous cap will occur as horizontal planes of equal concentrations, which can be tracked with a vertically oriented coordinate system. The shading in the sediment cap represents the presence of dissolved contaminants. As the contaminants are migrating upward from the sediment layer, the darker shading at the base of the cap depicts higher contaminant concentrations

metals, the source concentration can also be reduced by the cumulative loss of mass due to the migration of contaminants from the sediment layer. Over time, the processes outlined above can result in a reduction in the dissolved source concentration (C_o) in the pore water of the sediment layer.

For organic contaminants, decreases in the source concentration through time are often represented as first-order (exponential) decay processes and can be described by the equation

$$C_t = C_o e^{-\lambda t} \quad (1)$$

where

C_t = contaminant concentration at time t [M/L³]

C_o = initial contaminant concentration [M/L³]

λ = decay-rate coefficient [1/T]

t = elapsed time since decay began [T]

For magnitudes less than 0.5, the decay constant λ can be interpreted as being approximately equal to the fraction of the contaminant concentration that will decay in a unit of time (Chapra 1997).

First-order decay processes are associated with a set interval of time during which the contaminant concentration will decrease by 50 percent. This time interval is called the half-life ($t_{1/2}$) and is related to the decay-rate coefficient through the following relation:

$$t_{1/2} = \frac{\ln 2}{\lambda} \approx \frac{0.693}{\lambda} \quad (2)$$

At most contaminated sediment sites, the sorbed and dissolved contaminant concentrations as well as the geochemical conditions within the sediment layer vary both spatially and through time. Obtaining the field data necessary to quantify changes in the contaminant source concentration at a sediment site can therefore be difficult. Because of these challenges, source concentration changes should not be factored into performance predictions for a cap unless the loss mechanism(s) has been identified and the rate of loss has been quantified through analyses focused upon measurements made at the proposed capping site. This should include identification, measurement, and evaluation of products and geochemical parameters associated with contaminant source mitigation process(es). In general, decreases in the source concentration should be important only if the half-life associated with the contaminant concentration reductions is comparable to or less than the time the contaminant is expected to reside in the cap. In the absence of contaminant instabilities, source decay will be significant only in settings with rapid groundwater flow and rapid contaminant partitioning from the sorbed to the aqueous dissolved phase. Because of the difficulties, the authors recommend that a geochemist be consulted if contaminant source reduction is to be factored into the performance predictions for the cap.

Although solutions for exponentially declining source concentrations are common in the groundwater literature (U.S. Geological Survey (USGS) 1992, Zheng and Bennett 1995), source concentrations (C_o) in this report are assumed to be constant and independent of time. At a capping or natural recovery site, this is equivalent to assuming that the contaminant is stable in the sorbed and the dissolved phases, and that the contaminant losses due to transport during the interval of interest will not significantly reduce the contaminant concentrations in the sediment layer. This simplification reduces the complexity of the analysis and results in conservative contaminant loss predictions.

The assumption of a constant source concentration (C_o) is based upon the observation that many of the most problematic sediment contaminants, e.g., polychlorinated biphenyls (PCBs), are chemically stable, hydrophobic compounds that dissolve slowly in water and have aqueous solubilities that are orders-of-magnitude lower than sediment concentrations of environmental concern. These assumptions coupled with the low groundwater velocities found in most natural settings lead to the conclusion that a significant depletion of the contaminant concentrations in the sediment layer by advecting groundwater would require the passage of many pore volumes at solubility concentrations and therefore would entail extensive periods of time. Consequently, for many of the hydrophobic substances commonly associated with contaminated sediments, a constant source concentration would appear to be a reasonable simplification. As the contaminant migration rates due to diffusion are yet slower, a constant contaminant source concentration at sites dominated by diffusion also appears justified and will be assumed.

Contaminant Transport Mechanisms

Two phenomena drive the transport of the dissolved contaminants from the sediment deposit through the cap. The first is the movement of the contaminants by the bulk flow of groundwater and is termed advection. The second mechanism is hydrodynamic dispersion. Hydrodynamic dispersion represents the effects of diffusion and the effects of mechanical mixing associated with flow through a porous and permeable medium. Transport by diffusion is the result of random molecular motion and will result in the migration of contaminants even in the absence of groundwater flow. Mechanical mixing and diffusion cause the contaminant concentrations to increase gradually in the direction of transport. Each transport mechanism is described in a subsequent section of the report.

Many of the phenomena responsible for transport through the cap can be viewed as vector quantities. Vectors are associated with both a magnitude and direction. Given a horizontal sediment layer and an overlying cap, it is the vertical component of these vectors that will drive contaminants from the sediment layer upward through the cap. Throughout this report, the z -axis is assumed to be aligned with the vertical direction. Consequently, parameter values in the z or the vertical direction, and the vertical or the z component of the transport vectors, determine the performance of the cap and are emphasized in this report.

Molecular diffusion

Diffusion is a process whereby dissolved ionic and molecular materials move from areas of high to low concentration. In the presence of concentration differences, diffusion will transport contaminants through the subsurface even in the absence of groundwater flow. Driven by random molecular motion, diffusion can be visualized as the spread of a drop of ink in a motionless beaker of water (Figure 5). As the diffusion process proceeds, the ink will spread radially at the same rate in all directions and contaminate ever greater volumes of water. Because the ink is expanding radially, the volume of water associated with the ink will be spherical in shape until it is affected by the walls of the container. Although decreasing as diffusion proceeds, the highest concentration will remain at the center of the expanding sphere of ink-contaminated water.

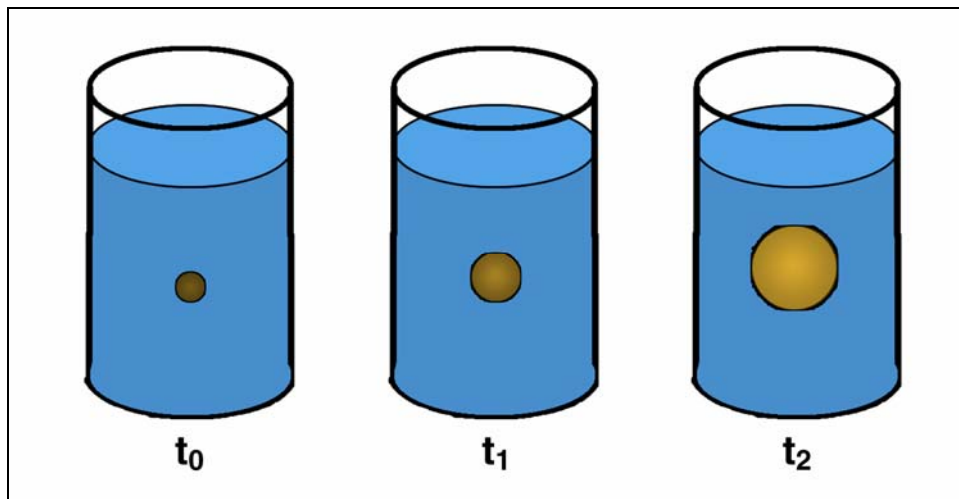


Figure 5. Diffusion: The results of diffusion as seen through the spread of a drop of ink in a beaker of motionless water. The t_0 represents the initial distribution of ink, while t_1 and t_2 represent the distribution at later times

Because of the spherical symmetry, the spatial distribution of ink can be represented by the changing ink concentrations with distance along any diameter of the sphere. The change in the ink concentration with distance along the diameter can in turn be described by a Gaussian (normal) curve (Figure 6). Like the process it describes, the Gaussian representation will evolve as diffusion proceeds. At any specific point in time, a different Gaussian curve will be needed to represent the distribution of ink within the expanding sphere of ink-tainted water. Reflecting spheres of ever greater volume, successive Gaussian curves will be wider at their base and have lower peak ink concentration. The increasing volume of ink-contaminated water coupled with the decreasing peak concentration reflects the

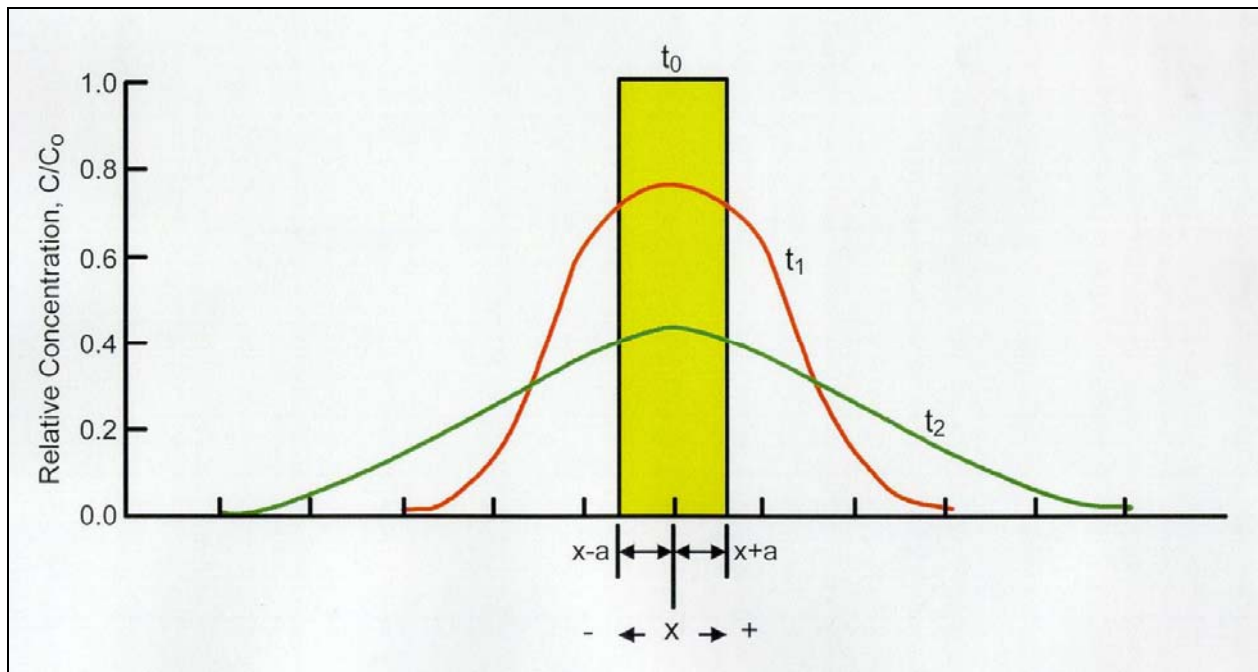


Figure 6. Gaussian Representation of a Diffusing Ink Drop: The initial width of the drop is $2a$, extending from $x-a$ to $x+a$. At any time t after the start of diffusion, the distribution of ink can be represented by a Gaussian or normal curve (from Fetter 1999)

fact that the mass of ink in the beaker does not change after initial placement of the ink.¹

This report assumes that the dissolved contaminant concentration within the pore space at the top as well as throughout the sediment layer equals the source concentration (C_o). In contrast, the initial dissolved contaminant concentration in the pore water of the cap is assumed to equal a background concentration of zero. In the presence of such concentration differences, diffusion will cause the migration of dissolved contaminants from the contaminated sediment layer vertically upward into the sediment cap. As diffusion moves the contaminant upward into the cap, a compensating contaminant mass sorbed to the sediment solids dissolves and maintains the dissolved concentration in the sediment layer at the source concentration (C_o). Assuming a background concentration of zero maximizes the rate of transport by diffusion and produces conservative estimates of cap performance.

Conceptually, the dissolved contaminants begin their journey into the cap from the top of a horizontal sediment layer (Figure 7). Along this horizontal plane the contaminant concentrations would abruptly change from C_o to the background concentration (presumed to be zero). As time advances and diffusion proceeds,

¹ Diffusion affects only the distribution and not the total mass of ink in the beaker, which is not altered after the initial placement of the ink drop. At any point in time during the diffusion process, the mass will equal a summation of the various concentrations (C_i) in the beaker multiplied by the volume of water at that concentration (V_i). The spatial distribution of C_i values is provided by the Gaussian curve.

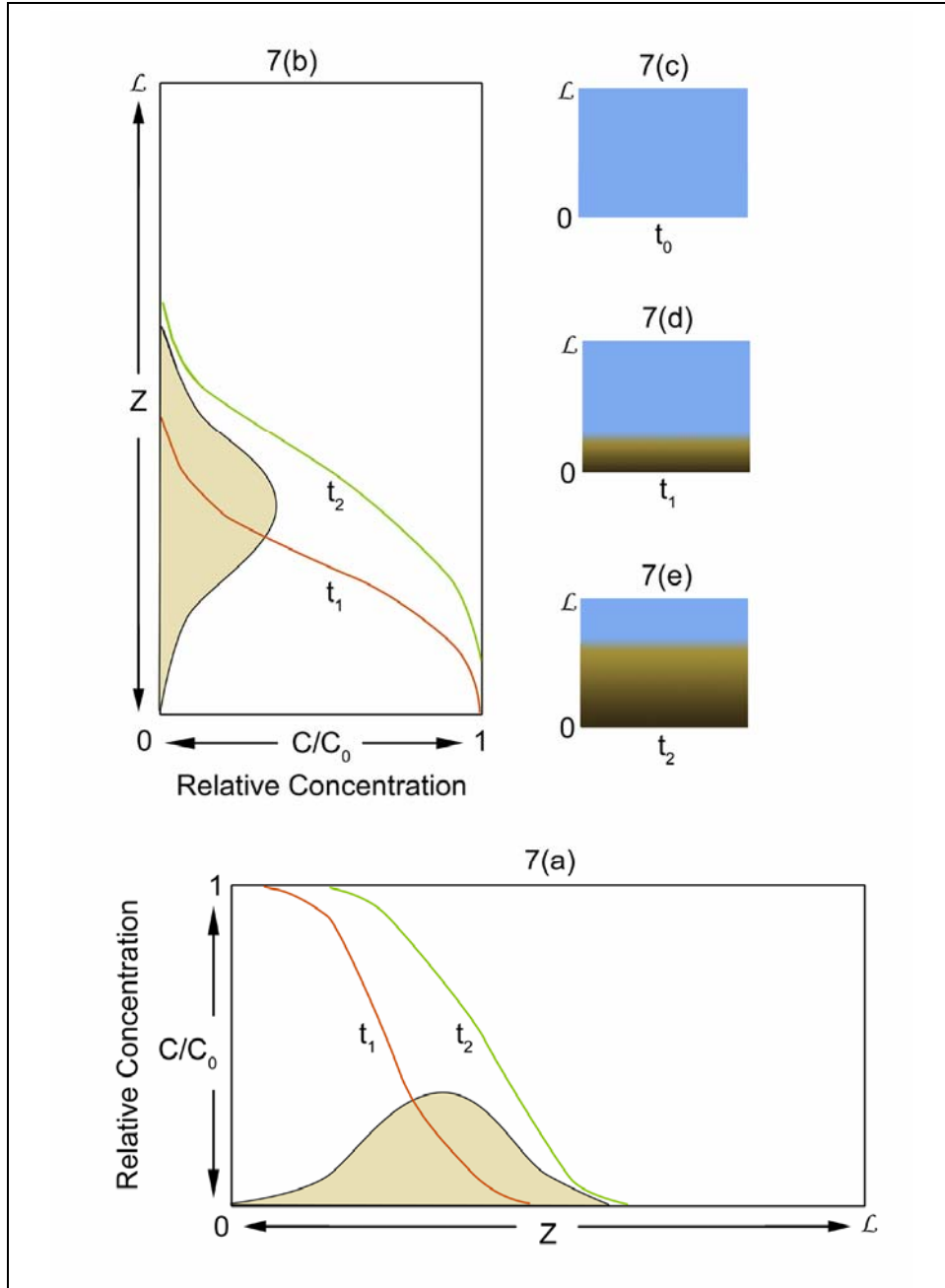


Figure 7. Sigmoidal Contaminant Distribution Along the Contaminant Front: Relationship between the Gaussian and sigmoidal distribution along the contaminant front is indicated in Figures 7(a) and 7(b) for time t_2 . Figure 7(a) depicts the contaminant front where the direction of interest is horizontal, while Figure 7(b) shows a similar depiction where the direction of interest is oriented vertically. Figures 7(c), 7(d), and 7(e) show the contaminant front at times t_0 , t_1 , and t_2 . At t_0 , the contaminant front is at the base of the cap, while t_1 and t_2 show the migration and lengthening of the contaminant front. All concentrations are normalized to the source concentration (C/C_0)

the initially abrupt concentration change will gradually moderate and evolve into an interval. This vertically aligned interval over which the contaminant concentration increases from the background concentration at the leading edge to the source concentration (C_o) at the trailing edge is called the contaminant front.

Like the ink in a motionless beaker of water, the length and shape of the contaminant front in the sediment cap will evolve as diffusion proceeds. However, in contrast, transport through the sediment cap is unidirectional and upward, with an unchanging maximum concentration equal to C_o (the source concentration) because of ongoing desorption and dissolution. Migration into and through the cap will result in the vertical movement of the entire contaminant front including its trailing edge at C_o , while the front's evolution will result in a continuous lengthening and change in shape. Upward movement of the evolving contaminant front can be tracked through the use of a 1-D coordinate system vertically oriented along the z -axis through the horizontal sediment cap (Figure 7). At any time, the vertical arrangement of contaminant concentrations along the front will follow a distribution that can be obtained from the Gaussian distribution used to describe the diffusing ink drop portrayed above. The contaminant distribution is developed from an approach that results in a cumulative summation of the area beneath an associated Gaussian distribution curve. This is depicted for time t_2 in Figure 7, where the associated Gaussian curve is also depicted. Assuming a background concentration of zero, this results in a sigmoidally shaped curve centered upon the curve's midpoint where the contaminant concentration would equal $C_o/2$.¹ As the position, length, and shape of the contaminant front within the cap is changing with transport, a different sigmoidal curve is needed to depict the contaminant distribution along the front at any time.

In many hydrogeologic settings, the principal direction of transport and interest is horizontal. This is reflected by Figure 7(a), where the distribution of contaminant concentrations along the contaminant front is shown as a function of horizontal distance. Figure 7(a) is consistent with the depictions provided in many hydrogeologic references (see for example Freeze and Cherry 1979, Domenico and Schwartz 1990, Fetter 2001), where the lateral migration of contaminants is stressed. In contrast, for capping and natural recovery problems, the direction of interest is oriented vertically upward through the cap. Vertically reorienting Figure 7(a) results in Figure 7(b). In Figure 7(b), the horizontal axis represents the contaminant concentration normalized to the source concentration (C/C_o), and the vertical axis represents the distance of transport. The top of the cap is located at L . As this document is devoted to describing the contaminant migration vertically upward through sediment caps, vertically oriented depictions of contaminant migration such as Figure 7(b) will be used throughout this report.

The mass of a contaminant transported by diffusion across a unit area in a unit of time is known as the diffusive flux. The diffusive flux in a given direction can be described by Fick's first law, which for 1-D transport can be stated as

¹ A contaminant concentration of $C_o/2$ also assumes the contaminant is chemically stable.

$$\text{Diffusive flux} = F = -D \left(\frac{dC}{dl} \right) \quad (3)$$

where

F = the mass of dissolved species crossing a unit area per unit time
[M/L²/T]

D = diffusion coefficient [L²/T]

C = dissolved species concentration [M/L³]

dC/dl = concentration gradient of the dissolved contaminant [(M/L³)/L]

The dissolved concentration of a contaminant (C), at a specific point in a contaminated sediment deposit or subaqueous cap, is a scalar quantity (a quantity that only has a magnitude associated with it). The concentration gradient (dC/dl) is the difference between dissolved contaminant concentrations (dC) at two points divided by their distance of separation (dl), when dl becomes very small. The concentration gradient (dC/dl) is a vector quantity (associated with both magnitude and direction). As exhibited by Equation 3, the diffusive contaminant flux (F) is directly proportional to both the magnitude of the diffusion coefficient (D) and the concentration gradient in the direction of interest. The diffusive flux (F) is the rate of mass movement caused by diffusion and is also a vector quantity oriented in the direction of the concentration gradient. The magnitude of F is the contaminant mass emitted per unit area per unit time.

In Equation 3, the negative sign is included to ensure that the diffusional flux is properly oriented with respect to the concentration gradient, i.e., from areas of high to low concentration. Without the negative sign, a negative concentration gradient would produce a contaminant flux in the positive direction. Conversely, a positive gradient would produce a flux in the negative direction. Such a result would contradict the observation that diffusion always occurs in the direction of decreasing concentration.

The diffusion coefficient (D) used above applies to the diffusional transport of a solute in a fluid and does not consider the complexities associated with diffusional transport in a saturated porous medium. D values for various compounds of environmental interest in water range from approximately 1×10^{-5} to 1×10^{-6} cm²/s at 25 °C and can be found in the literature (e.g., USEPA 1996b).

To account for the presence of the matrix solids in porous media, the diffusion coefficient must be modified and a related parameter called the effective diffusion coefficient (D_e) is used. The effective diffusion coefficient (D_e) factors in the need of the solute to move around the medium's matrix solids as diffusion proceeds. Because of the hindering effects associated with the presence of the matrix solids, the effective diffusion coefficient is always smaller than the diffusion coefficient ($D_e < D$). The relationship between the two coefficients can be expressed as

$$D_e = w D \quad (4)$$

where

w = coefficient that accounts for the porous medium, less than 1
[dimensionless]

D_e = effective diffusion coefficient [L^2/T]

The magnitude of D_e is a function of both the transporting medium and the contaminant. In the most general case, D_e is a second rank tensor usually represented as a 3×3 matrix (Bear and Verruijt 1987). However, in 1-D situations, D_e can be treated as a scalar constant, whose magnitude allows the diffusional contaminant flux to be equated to the concentration gradient in the direction of interest. For capping and natural recovery situations, D_e reflects the ability of the cap to transmit a contaminant vertically by diffusion and therefore will be denoted by D_{ez} in this report.

Diffusional transport upward through the cap would only occur over the fraction of the area consisting of fluid. For a cap composed of porous media, this area is equal to the porosity. The volume of a porous medium consists of the volume of the matrix solids composing the medium and the volume of the void or pore space existing between the solids.

$$V = V_s + V_v \quad (5)$$

where

V = porous medium volume (L^3)

V_s = volume of the matrix solids (L^3)

V_v = volume of the void space (L^3)

Porosity is defined as the volume of pore space divided by the total volume of the porous medium and, for this report, is viewed as a decimal fraction.

$$n = V_v / V \quad (\text{dimensionless}) \quad (6)$$

From the standpoint of transport through the cap, the vertical component of the concentration gradient and the resulting vertical diffusional flux are the parameters of interest. If the z-axis is oriented vertically upward through a planar-horizontal cap, the vertical component of the concentration gradient would be $(dC/dl)_z$ or dC/dz . Using the cap's porosity, the effective diffusion coefficient for the cap in the vertical direction (D_{ez}), and the vertical component of the concentration gradient, Equation 3 becomes

$$F_c = -n D_{ez} \left(\frac{dC}{dl} \right)_z = -n D_{ez} \left(\frac{dC}{dz} \right) \quad (7)$$

where

F_c = vertical diffusive contaminant flux [M/L²/T]

n = porosity [dimensionless]

D_{ez} = vertical effective diffusion coefficient [L²/T]

$(dC/dl)_z = dC/dz$ = vertical concentration gradient through the cap
[(M/L³)/L]

The porosity of a porous medium consists of interconnected pores through which contaminants can migrate as well as nonconnected pores that cannot act as conduits for the transport of fluids and contaminants. The portion of the porosity consisting of interconnected pore space is known as the effective porosity, which is defined as

$$n_e = \text{volume of interconnected pore space}/V \quad (\text{dimensionless}) \quad (8)$$

By definition, the magnitude of n_e must be less than or equal to the total porosity (n). For a sediment cap consisting of clean sand, most of the pore space should be interconnected and the effective porosity (n_e) and the total porosity (n) should be approximately equal. Replacing n with n_e in Equation 7 results in

$$F_c = n_e D_{ez} \left(\frac{dC}{dz} \right) \quad (9)$$

Equation 9 defines the vertical contaminant flux (the contaminant mass per unit surface area per unit time) driven upward through a sediment cap by the presence of a vertical gradient in the dissolved contaminant concentration where the effective porosity is approximately equal to the total porosity.

Equation 9 can be applied to steady-state scenarios, where the concentration gradient and therefore the diffusive flux are not changing with time, or at any given time during a transient (time-dependent) event. Transient events would include the evolution of the contaminant front during the diffusive transport of solutes through the cap with time. When used to predict cap performance, Equation 9 also implicitly presumes that groundwater flow is not a significant factor in the movement of the contaminants through the cap during the time interval of interest.

To obtain the contaminant mass passing through the entire surface of the cap, Equation 9 needs to be multiplied by the cap's surface area.

$$\text{Total vertical diffusive contaminant loading} = - D_{ez} n_e \left(\frac{dC}{dz} \right) A \quad (10)$$

where A is the area of the cap surface [L^2] and the units of vertical contaminant loading are mass per unit time [M/T].

Even at high concentration gradients, diffusion is a very slow mechanism for the transport of dissolved contaminants. From an environmental perspective, diffusion is the end-member of a transport continuum and represents the minimum rate of migration for dissolved contaminants through the saturated sediment cap. Despite this, transport by diffusion will always occur where concentration gradients are present and cannot be eliminated by judicious site selection or a sophisticated porous cap design. Therefore, even in the absence of groundwater flow, the vertical component of the concentration gradient will, over long periods of time, result in the migration of contaminants into and ultimately through the cap.

Further information regarding the process of diffusion in groundwater settings can be found in Domenico and Schwartz (1990), Fetter (1993), Zheng and Bennett (1995), and Freeze and Cherry (1979).

Advection

Advection is the bulk motion of water in response to an energy gradient. The total energy at a given location in a saturated porous medium is commonly expressed through the Energy (Bernoulli) Equation in terms of hydraulic head. For a fluid with constant density, and with pressure measured as gage pressure (pressure in excess of atmospheric), the Energy Equation has three components and can be written as

$$h = \text{elevation head} + \text{pressure head} + \text{velocity head} \quad (11)$$

$$h = z + P/\rho g + v^2/2g \quad (12)$$

where

h = total hydraulic head [L]

z = elevation of the point of head measurement [L]

P = pressure at point of head measurement [M/LT^2]

ρ = density of water [M/L^3]

g = gravitational acceleration [L/T^2]

v = fluid velocity [L/T]

Like the contaminant concentration at a given point in a cap, hydraulic head is a scalar quantity measured in terms of energy per unit weight and has units of length (energy/weight = force \times length/force = length). In the field, the elevation of the point of hydraulic head measurement (z) would be the height of the base of

a piezometer above an elevation reference datum. In hydrogeology, this reference datum is usually sea level. The pressure head represents the height to which water will rise in the piezometer above its base. In most hydrogeologic settings, the velocity of groundwater (v) is almost invariably small enough that the velocity head term can be ignored, reducing Equation 12 to (Figure 8)

$$h = z + \frac{P}{\rho g} \quad (13)$$

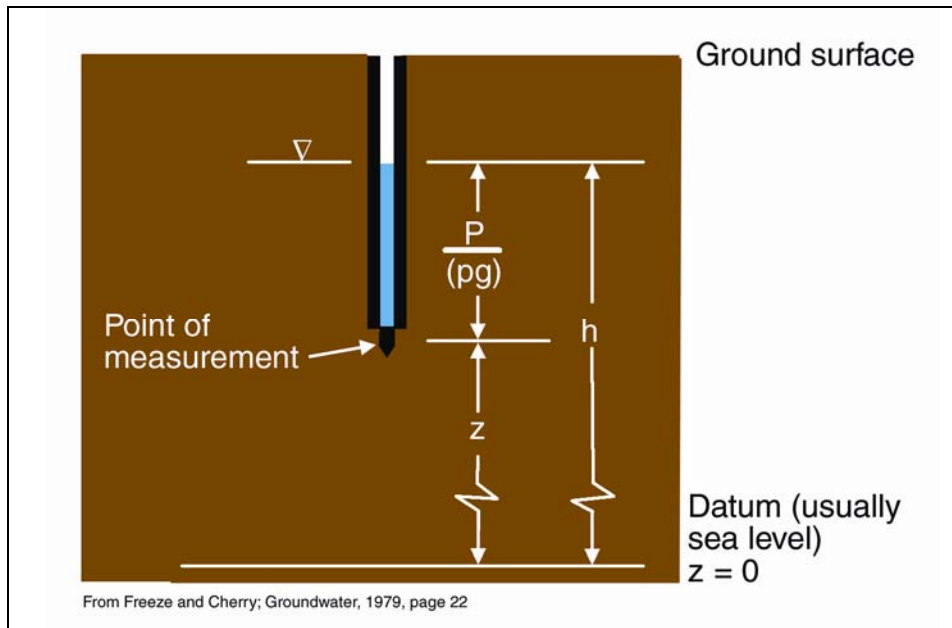


Figure 8. Components of Hydraulic Head in a Piezometer: Hydraulic head is a measure of the energy per unit weight at a point and has two components: elevation head (z) and pressure head ($P/(\rho g)$) (from Freeze and Cherry 1979)

For saturated media, the hydraulic gradient is defined as the difference in hydraulic head values (dh) between two locations divided by the separation distance between the two locations (dl). Like the concentration gradient, the hydraulic gradient (dh/dl) is a vector quantity. Groundwater will flow in response to a gradient in hydraulic head, moving from areas of high head to areas of low head. In many hydrogeologic settings associated with the presence of surface water, the magnitude of the hydraulic head increases with depth, resulting in a component of flow that is directed vertically upward. As noted, these settings are called groundwater discharge areas (Figure 9). For example, the difference between the hydraulic head value at the top of the cap and the hydraulic head value at the base of the cap divided by the cap's thickness gives the vertical energy or hydraulic gradient through the cap.

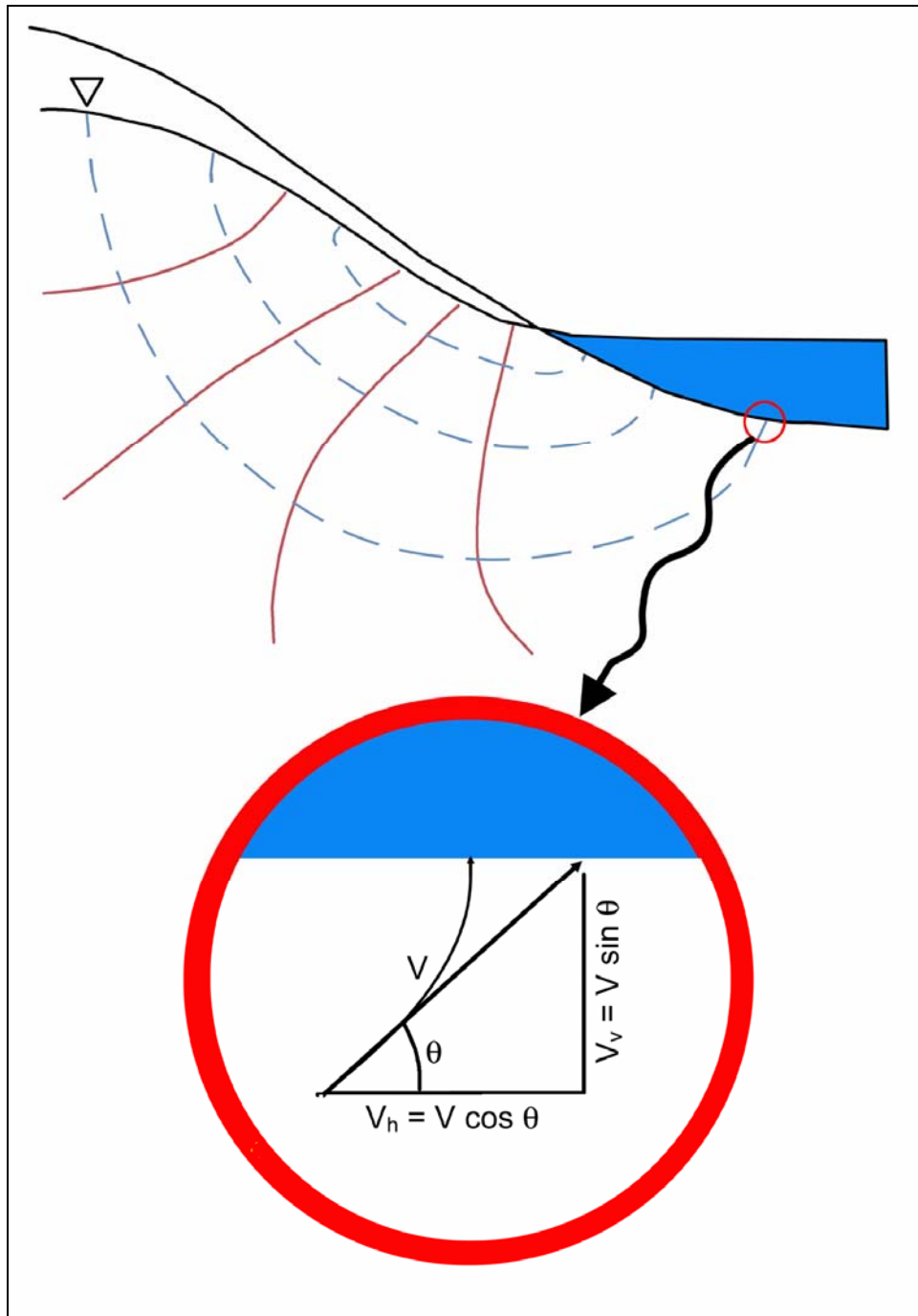


Figure 9. General Flow Lines and Equipotential Lines in Temperate Ground-water Discharge Areas: Groundwater motion at any point along a flow line (shown in red) can be depicted as a vector. The vector can be separated into horizontal and vertical component vectors. The upward vector component of the flow line is v_z . The vector's magnitude reflects the flux. Locations associated with equal hydraulic head values (equipotential lines) are depicted in blue. Note: vertical exaggeration enhances the appearance of V_v

Groundwater flow through a porous medium in a given direction is directly proportional to the hydraulic gradient and is generally quantified through Darcy's law. In 1-D, Darcy's law can be stated as

$$q = -K \left(\frac{dh}{dl} \right) \quad (14)$$

where

q = specific discharge, groundwater flux in the flow direction
[L³/(L²T) or L/T]

K = hydraulic conductivity [L³/(L²T) or L/T]

dh/dl = hydraulic gradient in the direction of flow [dimensionless]

As with Equation 3, the negative sign is included to ensure that the flow of groundwater is directionally oriented from locations of high to low hydraulic head.

Like the effective diffusion coefficient (D_e), in the most general case K is a second rank tensor. However for 1-D problems, K also reduces to a single-valued scalar coefficient, which relates the hydraulic gradient to the specific discharge in the direction of interest. For sediment caps, the direction of interest is vertically through the horizontal cap and K can be viewed as the ability of the cap to transmit contaminants upward by advection. The vertical hydraulic conductivity value responsible for transmitting contaminants through the cap by advection will be designated as K_z .

The specific discharge (q) represents the amount of groundwater passing through a unit of surface area per unit time. The unit of surface area is oriented perpendicular to the direction of groundwater flow under consideration. Specific discharge (also known as the Darcy Flux) has units, which can be reduced to a velocity. The specific discharge assumes that flow occurs through the entire cross section of the porous medium, whereas flow is actually limited to the space between the medium's particles or the pore space (Freeze and Cherry 1979). A more realistic flow velocity is the advective velocity, which is determined by dividing the specific discharge by the effective porosity:

$$v = \frac{q}{n_e} = -\frac{K}{n_e} \left(\frac{dh}{dl} \right) \quad (15)$$

where

v = advective velocity [L/T]

n_e = effective porosity [dimensionless]

Like the hydraulic gradient (dh/dl), both the specific discharge (q) and the advective velocity (v) are vector quantities. For capping and natural recovery, it

is the vertical component of the hydraulic gradient, specific discharge, and the advective velocity which are important for the performance of the cap. By inspection of both Equations 14 and 15, it is clear that the vertical component of the specific discharge and the advective velocity are directly proportional to the vertical component of the hydraulic gradient, and the magnitude of the hydraulic conductivity in the vertical direction (K_z). Again, assuming that the z -axis is oriented vertically,

$$v_v = \frac{q_z}{n_e} = -\frac{K_z}{n_e} \left(\frac{dh}{dl} \right)_z = -\frac{K_z}{n_e} \left(\frac{dh}{dz} \right) \quad (16)$$

where

v_z = vertical advective velocity [L/T]

q_z = vertical specific discharge, vertical groundwater flux [L/T]

K_z = vertical hydraulic conductivity [L/T]

$(dh/dl)_z = dh/dz$ = vertical component of the hydraulic gradient
[dimensionless]

Equations 14, 15, and 16 can be applied to steady-state groundwater-flow scenarios, where the hydraulic gradient (dh/dz) and therefore the specific discharge and the advective velocity are not changing with time, or at any given point in time during a transient (time-dependent) event. Transient events would be associated with a change in the hydraulic gradient with time at a given location in the groundwater-flow regime. Steady-state hydraulic gradients are seldom found in nature, where the stochastic nature of recharge events precludes such uniformity, and longer term cycles of rainfall and drought can be coupled to shorter term flow fluctuations. In addition, as the hydraulic conductivity (K or K_z) and the effective porosity (n_e) are included as constants, these equations also implicitly presume that the medium is uniform. Because of the ubiquitous presence of geologic heterogeneity and the associated large variation in the hydraulic properties of geologic materials, such uniformity is seldom realized. As a result, the specific discharge and the advective velocity will generally change over space and with time. In the field, the specific discharge and the advective velocity will generally depend upon the hydrogeologic setting, the location within the setting, and the point in time.

Ignoring the effects of diffusion or the mixing associated with fluid flow in porous media,¹ the contaminant concentration in the pore water of the cap would change abruptly from the background to the source concentration (C_o) with the passage of the contaminant front. This physically unrealistic, never observed advective transport process is sometimes referred to as “plug flow.” Plug flow conceptually assumes that all of the pore water in the medium is completely replaced with the passage of the contaminant front.

¹ This later effect is called mechanical mixing or mechanical dispersion and is discussed below.

The time required to move the contaminant front upward through the sediment cap by the advection of groundwater can be determined by dividing the thickness of the cap (\mathcal{L}) by the vertical advective velocity (v_z).

$$\text{Advective travel time} = \frac{\mathcal{L}}{v_z} \quad (17)$$

where \mathcal{L} = cap thickness [L]

The advective travel time needed for the contaminant to move through the cap is known as the breakthrough time (T_B).

In accordance with the assumptions associated with advective plug flow, once the contaminant moving vertically upward through the cap at velocity (v_z) reaches the top of the cap, the contaminant begins to be discharged to the overlying body of surface water at the source concentration, C_o .¹ Although describing only part of the transport process, these equations can be used to describe the advective transport of contaminants through a cap where the spreading of the contaminant front within the cap (due to diffusion and mechanical mixing) remains limited relative to the thickness of the cap during the time interval under consideration.

The groundwater flux passing vertically through the cap is the volume of groundwater exiting through a unit of the cap's surface area per unit time. As there is no consideration of groundwater storage, the flux from the top of the cap is assumed to be equal to the volumetric rate per unit area at which groundwater enters the bottom of the cap from the sediment layer. After breakthrough, the contaminant flux due to groundwater flow across a portion of the cap's surface a unit area in size would be

$$F_c = v_z n_e C_o \quad (18)$$

where

F_c = vertical advective contaminant flux [$M/L^2/T$]

v_z = vertical advective velocity [L/T]

C_o = source concentration [M/L^3]

After breakthrough, the advective rate of contaminant release to overlying surface water through the top of the cap can be obtained by multiplying the contaminant flux by the surface area of the cap:

¹ It should be noted, however, that in reality the contaminant front will widen because of the effects of diffusion and mechanical mixing and will cause contamination to move ahead of the distance predicted by considering advection alone.

$$\text{Total vertical advective contaminant loading} = F_c A = v_z n_e C_o A \quad (19)$$

where A is the surface area of the cap [L^2] and the units of contaminant loading through the cap due to groundwater flow are mass per unit time [M/T].

It should be noted that in some capping or natural recovery situations, the advective and diffusive transport mechanisms may not work in conjunction. For example, in groundwater recharge areas, the vertical component of the hydraulic gradient and the resulting flow of groundwater are directed downward (surface water discharging into the sediment layer). In these settings, the advective and diffusive transport processes will attempt to move the contaminants in opposing directions, and the vertical component of the hydraulic gradient will be directed downward while the vertical component of the concentration gradient will be directed upward.

Further information regarding the process of contaminant transport by advection in groundwater can be found in Domenico and Schwartz (1990), Fetter (1993), Zheng and Bennett (1995), and Freeze and Cherry (1979).

Assumptions associated with advective transport equations

Use of the advective transport equations presented above to predict the performance of a sediment cap relies upon several assumptions. Compliance with these assumptions will ensure that the placement of the capping layer will have a limited effect upon the local groundwater flow regime and that the advective velocities in the sediment layer and the overlying cap will be comparable. This in turn will allow the performance predictions for the cap to be generated from site-characterization data collected prior to cap placement (whether performed naturally or artificially) using the 1-D methods in this report. In contrast, if the cap is associated with a notably lower vertical advective velocity than exists within the sediment layer, the cap may cause a sizable portion of the groundwater to flow horizontally around the cap. In this case, the groundwater flow regime in the vicinity of the cap will be significantly altered, and the use of pre-cap site characterization data and the methods provided in this document for predicting cap effectiveness become problematic. Cap designs associated with a lower vertical advective velocity than currently found within the sediment layer may require the use of a numerical model to evaluate the potential importance of the horizontal flow component and assess cap effectiveness.

Capping proposals where the advective velocity within the cap would be lower than within the underlying sediment layer should not be encountered very frequently in practice. This assumption is based upon generalizations commonly associated with sediment deposits of environmental significance. Contaminated sediments generally accumulate in low-energy settings and tend to be fine-grained. Hydraulic conductivity in turn is directly proportional to the grain size of the medium, and lower values are therefore generally associated with fine-grained contaminated sediment deposits. In addition, hydraulic conductivity values exhibit a much wider variation than effective porosity values and therefore to a large extent control advective velocities in porous media (Equations 15 and 16).

As a result, contaminated sediment deposits are usually associated with relatively low advective velocities. Because contaminated sediments are capped artificially with a relatively coarse layer of sand (capping) or covered naturally with similar but uncontaminated materials (natural recovery), the hydraulic conductivity of the cover material should be comparable to or greater than the hydraulic conductivity of the underlying sediments. Given compliance with these assumptions, cap placement should have a limited effect on the local groundwater flow regime, and the methods provided in this report using site-characterization data collected prior to cap placement should allow the performance of the cap to be predicted.

Mechanical mixing

In porous media, the advective velocity (v) discussed above represents a velocity average. During the advection of solutes, velocity variations within the pores of a medium will cause half of the solute mass to travel faster and half to travel slower than the average advective velocity. Therefore, v represents the velocity at which the center of the contaminant front travels in the direction of transport. The spreading of the contaminant concentrations along the contaminant front during flow through porous media is brought about by the presence of the media solids. This phenomenon associated with advective velocity variations in porous media is called mechanical dispersion or mechanical mixing.

For many geological situations, mechanical mixing is a result of variations in advective velocity at both the pore scale, called microdispersion, and at a larger field scale due to variations in the material properties (heterogeneities), called macrodispersion. Variations in the advective velocity at the pore scale are caused by differences in the length of their flow paths, variations in pore size, and frictional flow effects (Figure 10). Variations in the advective velocities at the field scale are the result of differences in grain size and the degree of sorting, and consequently in the effective porosity and hydraulic conductivity values for the different materials in the direction of flow.

In most hydrogeologic situations, the flow-path lengths of interest and the almost ubiquitous presence of heterogeneities will cause the mixing effects due to macrodispersion to dominate over the effects associated with microdispersion. In contrast, most sediment cap thicknesses and therefore the flow-path lengths within the cap are on the order of a meter. This coupled with the relative homogeneity of many capping materials should in most settings cause the effects associated with macrodispersion to be limited. For sediment caps, consequently, macrodispersion can commonly be ignored and the effects of mechanical mixing can be approximated by considering microdispersion only.

As with diffusion, the effects of mechanical dispersion will cause a spreading of the dissolved contaminant concentrations along the contaminant front where the concentrations will range from the background concentration (presumed to be zero) at the front's leading edge to the source concentration (C_o) at the front's trailing edge. Like diffusion, the concentration distribution along a contaminant front will be sigmoidal and centered upon the average concentration ($C_o/2$),

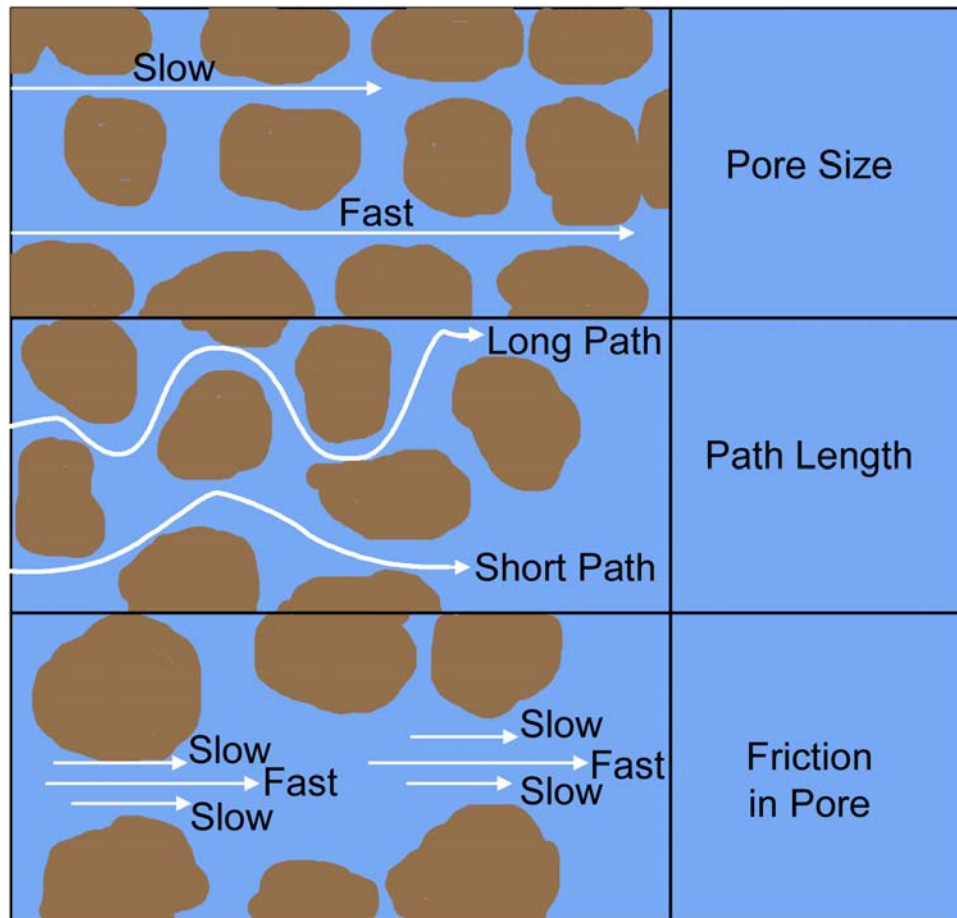


Figure 10. Causes of Mechanical Microdispersion: Pore-scale velocity variations that result in mechanical dispersion in the direction of flow (from Fetter 1999)

assuming the contaminant is stable). During advection, the entire contaminant front moves in the direction of flow with the center of the contaminant front (at concentration $C_o/2$) moving at the advective velocity v .

As before, the contaminant front can initially be conceptually viewed as consisting of a plane at the base of the cap over which the contaminant concentration abruptly changes from C_o to zero. With time, the contaminant front will move into the cap and moderate into an interval. As advection proceeds and the transport distance increases, so does the impact of mechanical mixing and the length of the contaminant front within the cap.

For 1-D analyses, the magnitude of mixing effects associated with mechanical dispersion is assumed to equal the product of the advective velocity (v , which can be viewed as the average or mean velocity) in the direction of interest and a parameter proportional to the length of the flow path. This relationship is intended to represent increases in velocity variations with increases in the flow-path length. The product is called the coefficient of mechanical dispersion.

$$\text{Coefficient of mechanical dispersion} = \alpha_L v \quad (20)$$

where

α_L = dynamic dispersivity in the direction of flow [L]

v = advective velocity [L/T]

For capping and natural recovery situations, the direction of interest is the vertical and the velocity component of interest is the vertical component of the mean advective velocity (v_z), and Equation 20 becomes

$$\text{Vertical coefficient of mechanical dispersion} = \alpha_L v_z \quad (21)$$

As noted, the magnitude of α_L is proportional to the length of the flow path, which for capping and natural recovery problems can be estimated from (Fetter 1999) as

$$\alpha_L = 0.0175 \mathcal{L}^{1.46} \quad (22)$$

where \mathcal{L} is the cap thickness in meters or feet [L].¹

Using this equation to determine α_L for a cap thickness of 1 m results in a value of 0.0175 m. This small value for α_L indicates that, for many capping and natural recovery scenarios, the vertical interval within the cap affected by mechanical mixing will be a small portion of the total cap thickness. Consequently, the significance of mechanical mixing at least for some caps may be limited.

The contaminant flux in the vertical direction through a porous cap due to mechanical mixing can be quantified as the product of a factor representing the magnitude of the mixing effects and the concentration gradient across the interval associated with the mixing.

$$F_c = -\alpha_L v_z n_e \left(\frac{dC}{dz} \right) \quad (23)$$

where

F_c = contaminant flux due to mechanical dispersion [$M/L^2/T$]

$\alpha_L v_z n_e$ = magnitude of the mixing effects [L^2/T]

dC/dz = vertical concentration gradient across the mixing interval
[$(M/L^3)/L$]

The rate of contaminant release due to mechanical dispersion across the entire cap surface to the overlying surface water would be

¹ Other equations to calculate α_L can be found in the literature (e.g., Fetter 2001).

$$\begin{aligned} \text{Contaminant loading due} \\ \text{to mechanical dispersion} \end{aligned} = F_c A = -\alpha_L v_z n_e \left(\frac{dC}{dz} \right) A \quad (24)$$

where A is the area of the cap surface [L²] and the units of total contaminant loading due to mechanical dispersion are mass per time [M/T].

Hydrodynamic dispersion

In real-world groundwater flow situations, the mixing effects of mechanical dispersion cannot be separated from the effects of diffusion. Therefore, the influences of these two mechanisms are combined in a parameter called hydrodynamic dispersion, D_L (Figure 11).¹

$$D_L = (D_e + \alpha_L v) \quad (25)$$

where D_L is the hydrodynamic dispersion coefficient [L²/T].

Like diffusion and mechanical mixing individually, hydrodynamic dispersion will cause a spreading of the contaminant along the contaminant front. Similarly, at any point in time, the distribution of the contaminant concentrations will be sigmoidal in shape and range from zero to C_o at the leading and the trailing edges of the contaminant front, respectively. The contaminant concentration at the center of the contaminant front will equal $C_o/2$ (again, assuming the contaminant is stable). As with mechanical mixing, the center of the contaminant front moves upward through the cap with advective velocity v_z . Addressing both the effects of diffusion and mechanical mixing, a cap performance analysis including hydrodynamic dispersion will exhibit an enhanced tendency for the contaminant front to lengthen during transport.

The effects of hydrodynamic dispersion are reflected in both laboratory and field where the passage of a solute front at a given point in a porous medium does not occur instantaneously. At any given location in a porous medium, passage of the solute front is commonly marked by a slow increase in the solute concentration over time. For sediment caps (as before), at the beginning of the transport process the contaminant front can be conceptually viewed as consisting of a horizontal plane at the base of the cap over which the contaminant concentration abruptly changes from C_o to zero. As flow is initiated and the contaminant front moves into the cap, the effects of hydrodynamic dispersion will cause the contaminant front to moderate and lengthen into an interval. As the transport process proceeds, the width of the contaminant front within the cap will lengthen.

¹ D_L is usually referred to in the literature as the longitudinal hydrodynamic dispersion coefficient and represents the effects of mechanical mixing and diffusion in the direction of transport. For flow in two or three dimensions, hydrodynamic dispersion can be defined for directions perpendicular or transverse to flow as well as parallel to the flow direction. Because this report considers solute transport in one direction only, the effects of transverse hydrodynamic dispersion are not discussed.

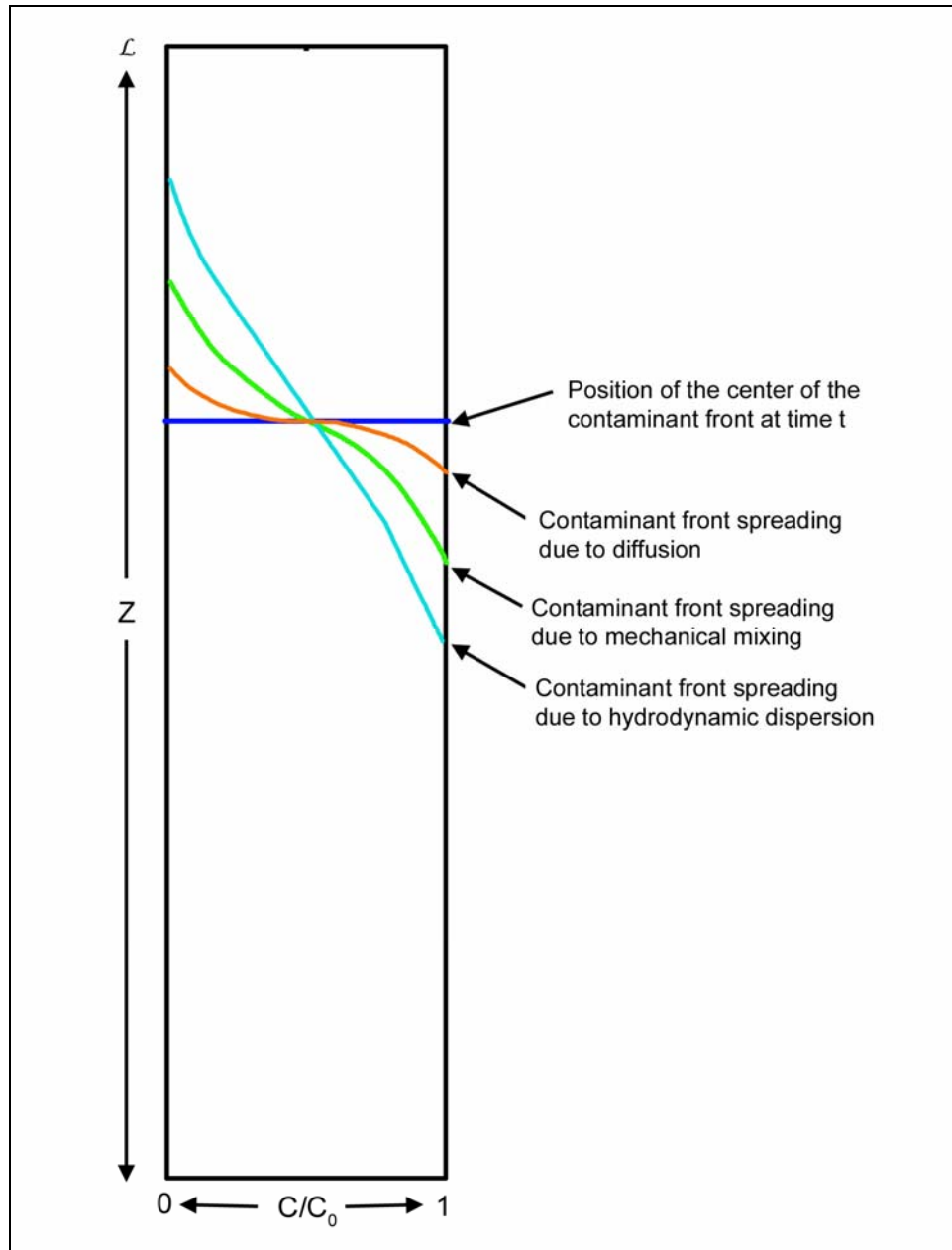


Figure 11. Hydrodynamic Dispersion: Hydrodynamic dispersion reflects the combined influences of diffusion and mechanical mixing (after Freeze and Cherry 1979)

The passage of the contaminant front will be reflected by a continuous increase in the dissolved contaminant concentration at any point within the cap over time. This will continue until the dissolved contaminant concentration equals C_o . When the contaminant front encounters the top of the cap, contaminants will start to be released to the overlying surface water. As the contaminant front continues its migration, the contaminant concentrations exiting through the cap will increase until the concentration equals C_o .

Modifying Equation 25 for sediment caps by replacing D_e with D_{ez} and the advective velocity v with the advective velocity component in the vertical direction (v_z) produces

$$D_{LZ} = (D_{ev} + \alpha_L v_z) \quad (26)$$

where D_{LZ} is the hydrodynamic dispersion coefficient in the vertical direction [L^2/T].

In settings that are approximately hydrostatic, the vertical component of advective velocity (v_z) will approach zero and the hydrodynamic dispersion coefficient is dominated by the effective diffusion term (D_{ez}). At higher advective velocities, the hydrodynamic dispersion coefficient is dominated by mechanical dispersion and the contribution of diffusion becomes secondary (Freeze and Cherry 1979). In either case, hydrodynamic dispersion causes the contaminant concentrations along the contaminant front to spread (Figure 11).

The vertical contaminant flux through a porous cap due to hydrodynamic dispersion can be quantified as the product of a factor representing the strength of the mixing effects due to diffusion as well as mechanical dispersion, and the concentration gradient across the interval associated with the mixing.

$$F_c = -D_{LZ} n_e \left(\frac{dC}{dz} \right) \quad (27)$$

where

F_c = hydrodynamic dispersive contaminant flux [$M/L^2/T$]

$D_{LZ} n_e$ = hydrodynamic dispersion contaminant mixing effect [L^2/T]

$\frac{dC}{dz}$ = vertical concentration gradient across mixing interval [$(M/L^3)/L$]

Using this equation, the vertical rate of contaminant release across the cap's surface to an overlying body of surface water due to hydrodynamic dispersion would be

$$\text{Hydrodynamic contaminant loading} = F_c A = D_{LZ} n_e \left(\frac{dC}{dz} \right) A \quad (28)$$

where A is the surface area of the cap [L^2] and the units of total hydrodynamic dispersive loading are mass per time [M/T].

Additional information regarding hydrodynamic dispersion can be found in Domenico and Schwartz (1990), Fetter (1993), Zheng and Bennett (1995), and Freeze and Cherry (1979).

Contaminant breakthrough and spatial distribution curves

As shown by Figures 7, 11, and 12, contaminant migration through sediment caps can be represented graphically in several ways. Contaminant-breakthrough curves (e.g., Figure 12a) depict the increase in the dissolved contaminant concentration at a given point in the cap (z) or at the top of the cap at \mathcal{L} over time with the passage of the contaminant front. Figures 7, 11, and 12b, in contrast, depict the distribution of dissolved contaminants with vertical distance through the cap at a specified point in time. Such a graph could be described as a spatial contaminant-distribution curve (Domenico and Schwartz 1990). In all of the figures, the horizontal axis represents the contaminant concentration normalized to the source concentration, C/C_o . In Figure 12a, the vertical axis represents time and T_B is the breakthrough time. For capping the natural recovery, T_B represents the length of time the contaminant front will reside within the cap. In Figures 7, 11, and 12b, the vertical axis represents the elevation (z value) of a given point within the cap above its base. The maximum value along the vertical axis is \mathcal{L} , the thickness of the cap.

Disregarding the mixing effects of hydrodynamic dispersion, the contaminant front would move upward through the cap at velocity v_z as a horizontal plane over which the contaminant concentration will abruptly change from the background to the source concentration (C_o). This is depicted in Figure 13, where the location of the contaminant front at several points in time (e.g., t_1 , and t_2) is represented as a horizontal line. Behind the contaminant front (beneath the horizontal line), the contaminant concentration equals C_o . Ahead of the contaminant front (above the horizontal line), the contaminant concentration equals the background concentration, which for simplicity is commonly assumed to equal zero. Contaminant breakthrough occurs when the contaminant front arrives at the top of the cap. In accordance with Equation 17, this occurs at a time equal to T_B or \mathcal{L}/v_z (Figure 13).

When hydrodynamic dispersion is included in the analysis, the contaminant concentration along the contaminant front no longer changes abruptly but gradually. Given a background concentration of zero, the contaminant front will be sigmoidal in shape and centered upon a contaminant concentration of $C_o/2$. The center of the contaminant front will arrive at the top of the cap at time \mathcal{L}/v_z . This occurs because the contaminant concentration equal to half the source concentration ($C_o/2$) travels upward through the cap with the vertical advective velocity of the groundwater (v_z). Contaminant concentrations less than $C_o/2$ arrive at the top of the cap prior to \mathcal{L}/v_z and concentrations higher than $C_o/2$ arrive at the top of the cap after \mathcal{L}/v_z (see Figure 11). With the passage of the contaminant front, the contaminant concentration equals C_o .

Contaminant transport: advection versus diffusion

The relative significance of contaminant transport by advection to transport by diffusion through a sediment cap of thickness \mathcal{L} can be expressed by a dimensionless parameter known as the Peclet number (P_e). The Peclet number can represent a ratio of the effectiveness of these two mechanisms and therefore provides a

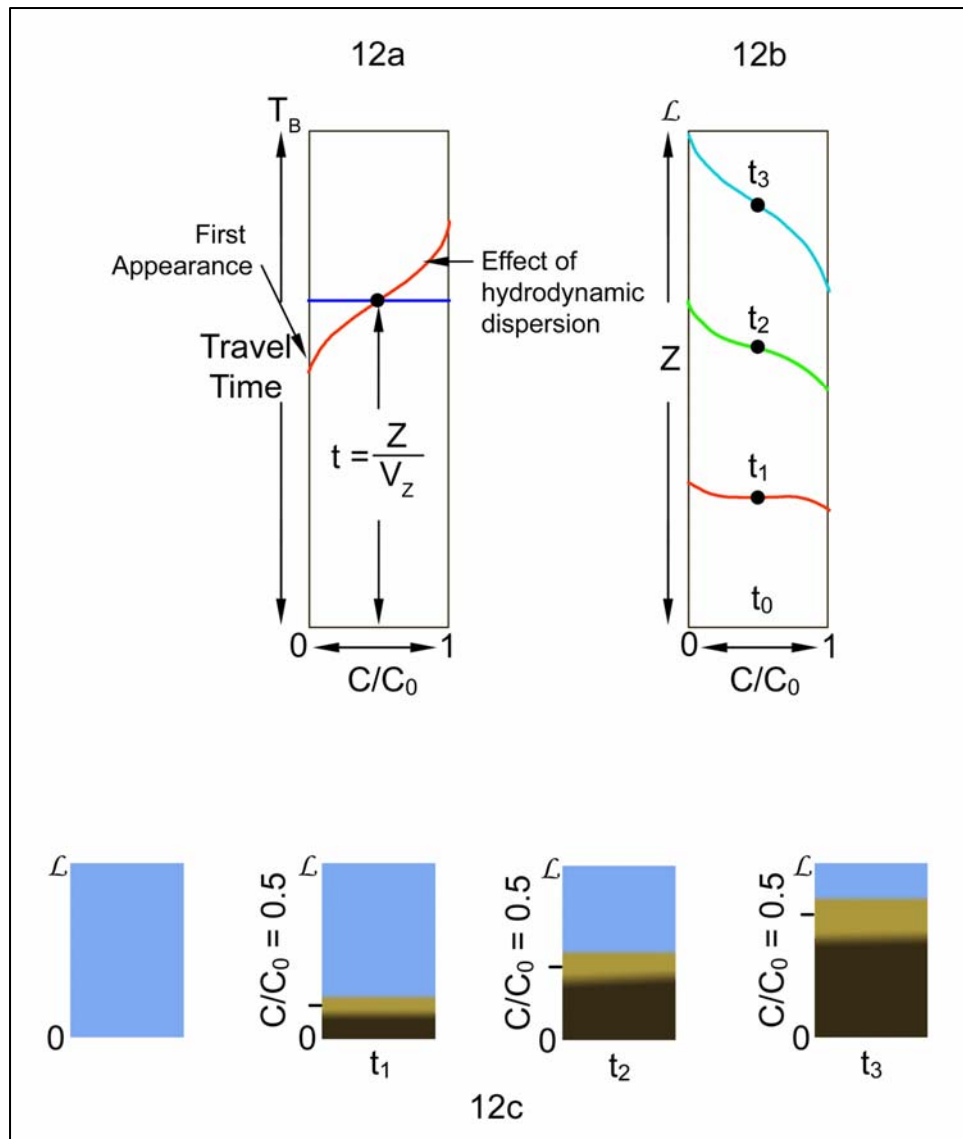


Figure 12. Contaminant Breakthrough and Distance Curves: Figure 12a depicts the concentration increase observed at a given point (z) in the cap through time while 12b depicts the concentration distribution along the contaminant front at different points in time (t_0, t_1, t_2, t_3). The “dot” represents the center of the contaminant front (where C/C_0 equals 0.5), which travels at v_z . The distance of transport (z) equals the product of v_z and the time of transport (t). Figure 12c is a cross section showing the migration and lengthening of the contaminant front through the cap with time (after Freeze and Cherry 1979)

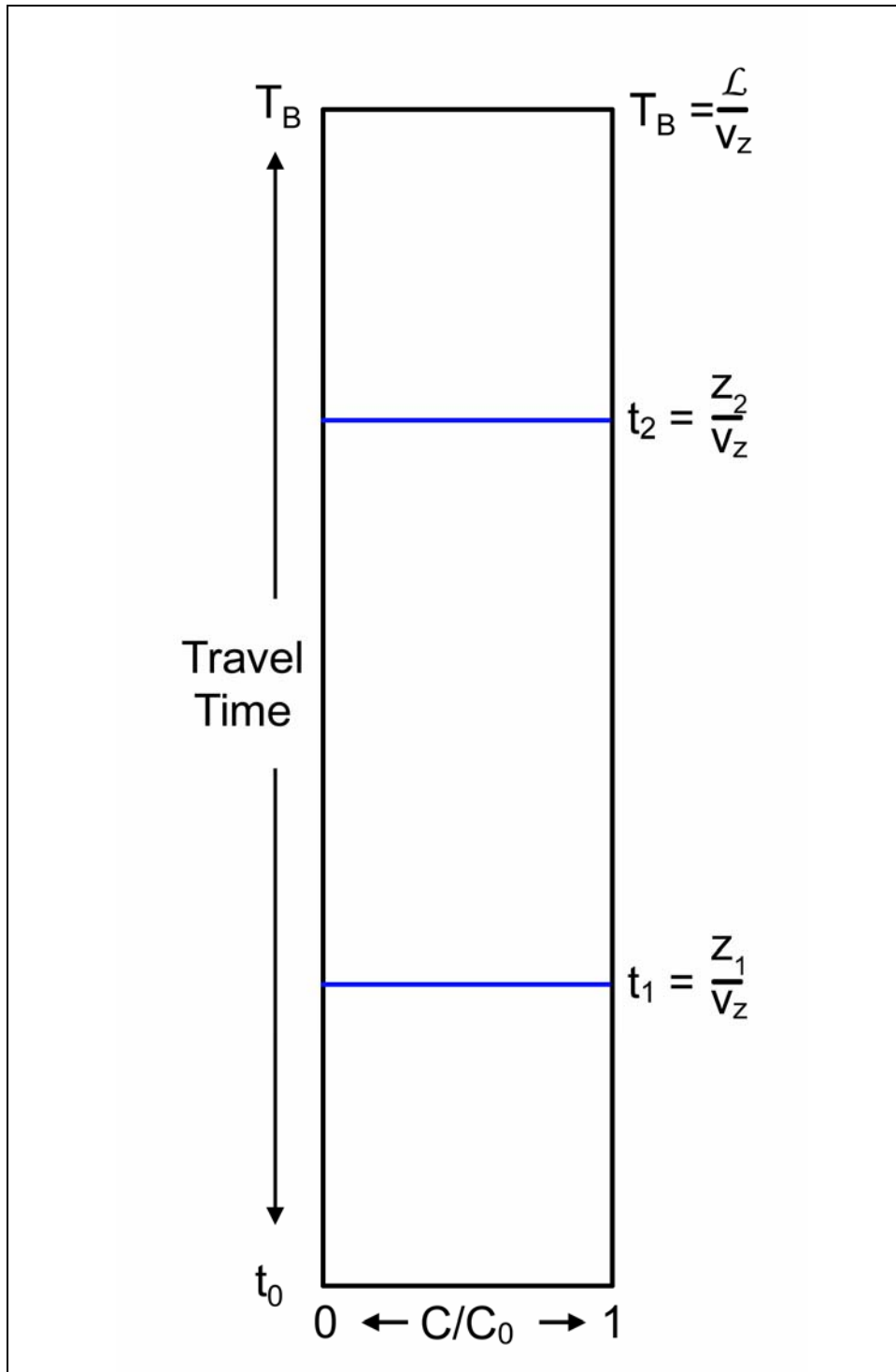


Figure 13. Advective Transport: Ignoring mechanical dispersion, the contaminant front will move vertically upward through the cap as a horizontal plane at velocity v_v , assumed to be a constant. As the cap thickness (\mathcal{L}) is a constant, the breakthrough time (T_B) equals \mathcal{L} / v_v (after Freeze and Cherry 1979)

comparison of their importance in transporting dissolved constituents (Freeze and Cherry 1979). For capping and natural recovery problems, P_e can be defined as

$$P_e = \frac{q_z}{n_e} \left(\frac{\mathcal{L}}{D_{ez}} \right) = v_z \left(\frac{\mathcal{L}}{D_{ez}} \right) \quad (29)$$

where

q_z = vertical specific discharge [L/T]

n_e = effective porosity [dimensionless]

\mathcal{L} = cap thickness [L]

D_{ez} = vertical effective molecular diffusion [L^2/T]

v_z = vertical advective velocity [L/T]

The Peclet number is directly proportional to both the advective velocity and the flow-path length under consideration. For capping and natural recovery problems, the flow-path length is determined by the cap's thickness. The limited thickness of most sediment cover layers (on the order of 1 meter) accounts for the emphasis given in this document to the processes associated with microdispersion and will lower the magnitude of the Peclet number for most capping and natural recovery proposals.

In hydrogeologic settings where the value of the Peclet number is 1, the processes of diffusion and advection are of equal importance in moving the contaminant through the medium, and neither mechanism dominates transport. In hydrogeologic settings in which the Peclet number is determined to be less than 1, transport is dominated by molecular diffusion. In these settings, the relative significance of diffusion over advection will increase as the magnitude of the Peclet number decreases from 1. Under hydrostatic conditions, groundwater is motionless (stagnant), and the hydraulic gradient (dh/dl), the advective velocity (v_z), the specific discharge (q), and therefore the Peclet number (P_e), are all zero. In general, predictions of contaminant transport driven solely by diffusion are appropriate only for geologic settings associated with very low hydraulic conductivity values or in which hydrostatic conditions prevail throughout the time interval of interest (Fetter 1993).

In hydrogeologic settings, in which the Peclet number is determined to be greater than 1, groundwater flow or advection dominates transport (Fetter 1993, USEPA 1996a). The relative dominance of advection over diffusion in this case is proportional to the extent beyond which the Peclet number (P_e) exceeds 1. At many contaminated sediment sites, the transport through the cap will be dominated by advection and Peclet numbers in excess of 1 should be anticipated.

It should also be noted that, in most hydrogeologic settings, the value of the Peclet number will vary with time. This occurs because of the stochastic nature of precipitation events, which will generally cause notable variations in the magnitude, and occasionally even in the direction of the hydraulic gradient and,

therefore, of groundwater flow. Velocity variations can also include intervals during which the hydraulic gradient and therefore the groundwater velocity will approach zero and conditions will be approximately hydrostatic. During such times, the Peclet number will become less than 1 and contaminant transport would be driven primarily by diffusion. However, the overall diffusional contribution to transport during these static intervals can be limited when compared with the advective contribution associated with the periods of active groundwater flow. Additionally, in hydrogeologic settings where the periods of advection are limited and intermittent, and diffusion is generally the dominant mechanism of transport, the cumulative effects of diffusional transport can be rapidly overwhelmed by an advective event of much shorter duration.

Overview of Contaminant Sorption

Because of the limited thickness of most sediment caps, contaminant sorption can be a critical mechanism in their performance. The term sorption covers a variety of processes including adsorption, chemisorption, absorption, and ion exchange (Fetter 1993). Through these processes, a portion of the dissolved contaminant(s) is removed from solution and attached to the adjacent cap solids. When the contaminant is sorbed on the matrix solids of the cap, it is unaffected by the hydraulic and concentration gradients present in the pore water. While in solution, however, it is subject to transport by the bulk movement of the groundwater and to spreading by mechanical mixing and diffusion. As contaminants can spend a large portion of their time bound to the cap solids, sorption can reduce the effectiveness of contaminant transport by orders-of-magnitude.

In the absence of contaminant sorption, the performance of the cap will generally be determined by the presence or absence of groundwater flow. Sediment caps with a limited sorptive capability and placed in settings associated with an upward advective flow component will have a limited effect on the migration and release of dissolved contaminants to the overlying body of surface water. This occurs because cap thicknesses are usually measured in terms of a meter or less, and therefore the cap constitutes no more than a thin veneer over the underlying groundwater flow system.

Though sorptive mechanisms can be very complex, this document considers them in their simplest form. This approach presumes the existence of a rapid, linear, and reversible relationship between equilibrium contaminant concentrations in the pore water and the sorbed contaminant phase associated with the solids of the cap. The assumption of equilibrium is generally appropriate when the rate of contaminant exchange between pore water and the medium solids is rapid relative to the rate of contaminant movement through the medium. A linear relationship between the pore-water concentration and the contaminant concentration sorbed to the matrix surface generally is acceptable if the pore-water concentration is low relative to the sorptive capacity of the matrix. Reversibility presumes that the contaminants are equally adept at both adsorbing and desorbing from the cap solids. Transport equations incorporating nonequilibrium sorption, nonlinear sorption, or adsorption/desorption hysteresis are more complex (USGS 1992).

For a more complete discussion of contaminant sorption and partitioning, refer to Domenico and Schwartz (1990), Fetter (1993), Zheng and Bennett (1995), and USEPA (1999).

The sorptive tendency of a contaminant can be expressed by a dimensionless parameter called the retardation coefficient, which can be incorporated directly into the transport equations previously discussed. In the presence of groundwater flow, the retardation coefficient can be quantified as the ratio of the advective velocity of groundwater (v , Equation 15) to the reduced advective velocity that a contaminant would experience due to sorption (v_c).

$$R = \frac{v}{v_c} \quad (30)$$

where

R = contaminant's retardation coefficient [dimensionless]

v = advective velocity of groundwater [L/T]

v_c = reduced advective velocity of the contaminant due to sorption [L/T]

For nonsorbing contaminants, the magnitude of R equals 1 and v_c would equal v . For sorbing contaminants, v_c will always be less than v and R will exceed 1.

When Equation 30 is rearranged for v_c ,

$$v_c = \frac{v}{R} \quad (31)$$

The variable v_c represents the reduced advective velocity of a contaminant due to its tendency to sorb to the solids of the cap. For example, a retardation factor of 2 implies that a contaminant would spend only half of its time in solution and subject to movement by energy and concentration gradients and half of its time sorbed and immobile.

For 1-D advective transport vertically upward through the cap, the vertical component of the advective velocity (v_z) is the velocity component of interest and Equation 31 becomes

$$v_{zc} = \frac{v_z}{R} \quad (32)$$

where v_{zc} is the reduced advective velocity of the contaminant in the vertical direction due to sorption [L/T].

The breakthrough time (T_B) for a contaminant driven through the cap by advection and interacting with the cap solids through sorption with a retardation coefficient equal to R would be

$$T_B = \frac{\mathcal{L}}{v_z / R} = \frac{\mathcal{L}}{v_{zc}} \quad (33)$$

where \mathcal{L} is the cap thickness [L].

For sorbing contaminants, Equation 33 provides an estimation of the time that the contaminant front will reside within the sediment cap, when driven primarily by groundwater flow, and the effects of mechanical mixing and diffusion can be ignored.

In a similar manner, R can be incorporated into the 1-D transport equations for diffusion and hydrodynamic dispersion. For a sorbing contaminant migrating vertically through the cap by diffusion, the vertical effective diffusion coefficient (D_{ez}) would be divided by R to give D_{ez}/R . As R exceeds 1 for sorbing contaminants, D_{ez}/R expresses the reduced tendency for sorbing contaminants to migrate by diffusion. To represent the impact of sorption on the mixing effects due to hydrodynamic dispersion for a contaminant moving vertically upward through the cap, the vertical hydrodynamic dispersion coefficient (D_{Lz} , Equation 26) would also be divided by R to give D_{Lz}/R . In turn, D_{Lz}/R represents the tendency of contaminants that sorb to disperse and/or diffuse at a slower rate than contaminants that do not interact with the cap solids. Because of these effects, at any given point in time, the contaminant front of a sorbing contaminant will be thinner and lag behind the contaminant front of a solute that does not sorb (Zheng and Bennett 1995) (Figure 14).

The retardation coefficient can be related to the properties of the sediment cap and the characteristics of the contaminant through the equation

$$R = 1 + \left(\frac{\rho_b}{n_e} \right) K_d \quad (34)$$

where

R = retardation factor [dimensionless]

ρ_b = bulk density of the cap [M/L³]

n_e = effective porosity of the cap [dimensionless]

K_d = partition coefficient of the contaminant [L³/M]

The partition coefficient (K_d) is an equilibrium constant that presumes a linear relationship between the dissolved concentrations of the contaminant and the sorbed concentrations. The magnitude of K_d will be controlled by the chemical properties of the contaminant, the site water, and the cap solids. For a sediment cap, K_d is defined as the ratio of the contaminant concentration associated with the

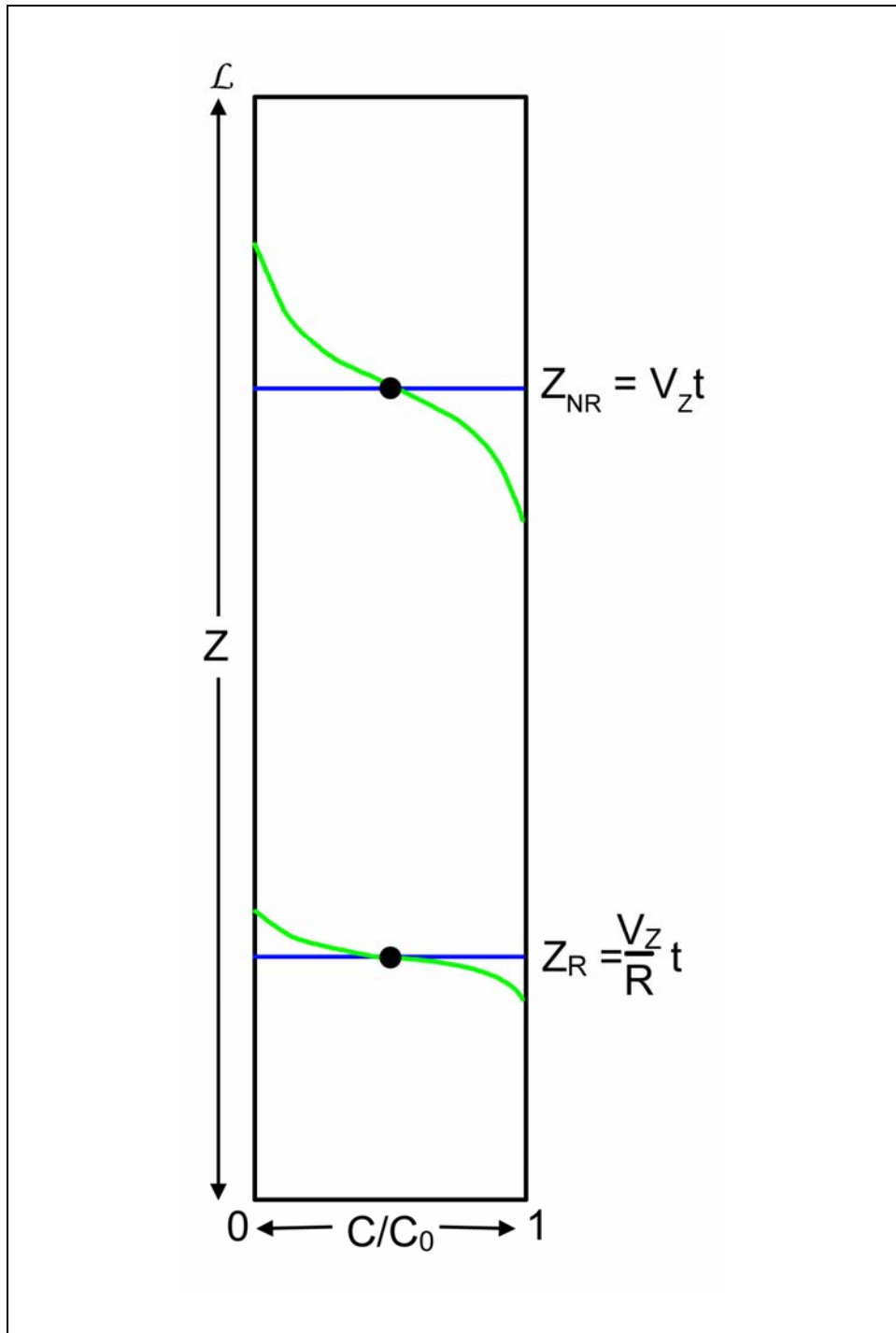


Figure 14. Contaminant Fronts for Retarded Versus Nonretarded Contaminants: Sorbing contaminants have lower rates of advection and hydrodynamic dispersion and, therefore, narrower fronts, which lag behind nonretarded contaminants at any transport time t (after Freeze and Cherry 1979)

cap solids to the contaminant concentration in the adjacent aqueous solution under equilibrium conditions. For example, for the reversible reaction



where

C_{aq} = concentration of the dissolved contaminant at equilibrium [$\mu\text{g/ml}$, M/L^3]

C_s = concentration of the contaminant sorbed to the cap solids [$\mu\text{g/g}$, M/M]

The partition coefficient for this reaction would be

$$K_d = \frac{C_s}{C_{aq}} \quad (36)$$

where K_d is the partition coefficient [ml/g , L^3/M].

Some care and consideration should be given to the K_d value selected for use in Equation 34, as K_d values vary greatly. Given the potential for error, for natural recovery proposals, K_d values should be determined from the site characterization data. For engineered caps, K_d quantification will need to include an analysis of both the site characterization data and the cap design parameters. It should also be noted that using one value for K_d and R presumes that the cap is homogeneous and that the retardation characteristics are uniform throughout the volume of the cap.

Hydrophobic organic contaminants

Two methods are presented below for obtaining K_d values for hydrophobic organic compounds. These methods are predicated upon the high affinity of hydrophobic compounds for organic material and their low solubility in water. Consequently, it is presumed that the sorption processes, the magnitude of K_d , and therefore the retardation coefficient (R) are controlled by the organic content of the cap. Both approaches assume that the cap's K_d can be equated to the product of a second partition coefficient (K_{oc}) and the organic carbon content of the cap,

$$K_d = f_{oc} K_{oc} \quad (37)$$

where

K_{oc} = partition coefficient relating the contaminant concentrations sorbed to the organic material of the cap and in solution [mg/l , M/L^3]

f_{oc} = mass fraction of organic carbon in the sediment cap [mg/mg , dimensionless]

The coefficient K_{oc} in turn is defined as the ratio of the contaminant concentration sorbed to a granular organic carbon medium to the contaminant concentration dissolved in an adjacent aqueous phase at equilibrium (Zheng and Bennett 1995).

The first approach quantifies the value of K_{oc} for a specific organic contaminant through its relationship to a laboratory-derived parameter known as octanol/water partition coefficient (K_{ow}). The K_{ow} is the ratio of the mass of the compound under consideration that dissolves in octanol to the mass of the compound dissolved in the water in a mixture of the two at equilibrium. Values of K_{ow} for most hydrophobic substances of environmental concern have been measured and are available in the technical literature, e.g., Suthersan (1997) and USEPA (1996b). The relationship between K_{oc} and K_{ow} has been empirically defined through a variety of regression-derived expressions (Fetter 1993), which can be generalized as (Zheng and Bennett 1995)

$$K_{oc} = \phi (K_{ow})^\psi \quad (38)$$

or

$$\ln K_{oc} = \ln (\phi) + \psi \ln K_{ow} \quad (39)$$

where (ϕ) and (ψ) are compound-specific empirically derived parameters [dimensionless].

A second approach relates the value of K_{oc} to the aqueous solubility of the compound under consideration through the expression (Zheng and Bennett 1995)

$$K_{oc} = f S^k \quad (40)$$

or

$$\ln K_{oc} = \ln f + k \ln S \quad (41)$$

where

f and k = compound-specific experimentally derived parameters
[dimensionless]

S = solubility of the compound in water [M/L³]

Solubility values (S) for hydrophobic compounds of environmental interest have been measured and are also available in the literature, e.g., Suthersan (1997).

For an engineered cap, estimates for ρ_b , n_e , and f_{oc} would be set by the design criteria for the cap. For a natural recovery proposal, these values would need to be obtained from field data at the contaminated sediment site. A K_{oc} estimate can be obtained above from Equations 38 through 41 relating K_{oc} to K_{ow} or S . Once values for K_{oc} and f_{oc} are determined, Equation 33 can be used to determine K_d .

Along with values for ρ_b and n_e , K_d can be placed in Equation 30 to obtain an estimate for the retardation coefficient R .

Most authors note the existence of a threshold f_{oc} , below which the method presented above to predict the sorptive behavior of hydrophobic compounds becomes problematic (Fetter 1993, Domenico and Schwartz 1990, Zheng and Bennett 1995). For example, the threshold f_{oc} has been cited by Zheng and Bennett (1995) to be as low as 0.01 percent. For subaqueous caps with f_{oc} values below this threshold, the sorptive contributions of the matrix become comparable to the sorptive contribution of the f_{oc} (Fetter 1993, Domenico and Schwartz 1990). The sorptive ability of a sediment cap consisting exclusively of sand and silt-sized quartz generally is not considered significant, and would in most situations do little to retard the migration of organic contaminants through the cover layer.

Implicit in the method presented for determining R is the assumption that carbonaceous material (f_{oc}), which dominates the sorptive processes, is uniformly distributed throughout the volume of the cap. A heterogeneous f_{oc} distribution would be associated with locations of lower f_{oc} values and a lower sorptive capability. These sites would act as preferred pathways for the migration of the contaminants upward through the cap.

The methods outlined above are most reliable for nonpolar, hydrophobic organic contaminants, including many chlorinated solvents, pesticides, and PCBs. For hydrophobic contaminants, retardation factors can be very large, indicating that the contaminant would spend most of its time sorbed to the cover matrix. For capping and natural recovery problems, contaminants that aggressively interact (sorb) with a sediment cover will reside within the cap for longer periods of time, significantly increasing the time needed for breakthrough.

Metal contaminants

Because of their tendency to give up electrons, metals commonly form cations when dissolved in an aqueous solution. As water is a polar solvent, the solubility of charged species such as cations is generally much greater than the solubility of the uncharged, nonpolar (hydrophobic) organic compounds discussed previously. Dissolved metals can interact with cap solids through several mechanisms, including cation exchange. Cation exchange is the replacement of a cation attached to the surface of a solid with a cation in solution. For example, the exchange reaction between two cations generically identified as A and B would be



where

a = valence for cation A

b = valence for cation B

$bA-X$ = sorbed cation A to matrix solid X

$aB-X$ = sorbed cation B to matrix solid X

Obtaining acceptable K_d values for metal contaminants is notably more challenging than for the sorption of nonpolar, hydrophobic organic compounds, which can be equated to the product of a contaminant-specific partitioning factor (K_{oc}) and the organic content (f_{oc}) of the cap. As with hydrophobic contaminants, the K_d concept for metals assumes that only trace concentrations of the contaminant are present in the dissolved phase. However, given the high solubilities of metals in water, this assumption becomes problematic.

For metals sorbing to the matrix solids of a cap through cation exchange, K_d values can vary greatly depending upon the contaminant, the chemistry of the aqueous phase, the nature of the cap solid, and the method of measurement (USEPA 1999). Further complications include the finite capacity of the matrix solids to participate in the sorption reactions and the need to consider all of the species in solution competing with the cation of concern for the solid's sorption sites. To address the latter factor requires knowledge defining the valence and distribution of the chemical species in the pore water of the sediment layer, information not commonly collected at sediment remediation sites.

Several expressions defining R for exchanging cations are provided in the literature (USGS 1984, Domenico and Schwartz 1990). These expressions for R depend upon the valence of the cations participating in the cation exchange process. Subject to many of the limitations noted above, these expressions become more involved with increasing valence and where the exchanging ions differ in valence.

Because of the challenges noted above, the authors recommend that a geochemist be consulted if the retardation effects for metals contaminants are to be included in the performance prediction of the cap. Capping proposals that rely upon the retardation effects of metal contaminants should include an assessment of the assumptions, limitations, and uncertainties associated with the R value used in the proposal. Details regarding cation exchange are provided in Garrels and Christ (1965) and Appelo and Postma (1996). Information on retardation coefficients and cation exchange is provided in USGS (1984), Zheng and Bennett (1995) and USEPA (1999).

Contaminant Flux Equations

The mass of contaminant migrating across a unit of surface area in a unit of time defines the contaminant flux. Although discussed separately, contaminant flux generally consists of the combined contributions of advection (Equation 18) and hydrodynamic dispersion (Equation 27). For contaminant migration in the vertical direction, the contaminant flux would be

$$F_c = v_z n_e C - D_{LZ} n_e \left(\frac{dC}{dz} \right) \quad (43)$$

where

F_c = advective and hydrodynamic dispersive contaminant flux
[M/L²/T]

$v_z n_e C$ = advective contaminant flux [M/L²/T]

$D_{LZ} n_e (dC/dz)$ = hydrodynamic dispersive contaminant flux [M/L²/T]

v_z = vertical advective velocity [L/T]

n_e = effective porosity [dimensionless]

C = aqueous contaminant concentration [M/L³]

D_{LZ} = vertical hydrodynamic dispersion coefficient [L²/T]

dC/dz = vertical concentration gradient [(M/L³)/L]

As before, the negative sign in Equation 43 placed before the hydrodynamic dispersion term ensures that the hydrodynamic dispersive flux is from areas of high to low concentrations.

For sorptive contaminants, the vertical advective velocity (v_z) and the coefficient for the vertical hydrodynamic dispersion (D_{LZ}) would be divided by R , the contaminant retardation coefficient, to give

$$F_c = \frac{v_z}{R} n_e C - \frac{D_{LZ}}{R} n_e \left(\frac{dC}{dz} \right) \quad (44)$$

For a sorbing contaminant, R would exceed 1 and F_c would be less than the value for a nonsorbing contaminant. As noted, R is dimensionless.

To obtain an estimate of the contaminant mass passing through a sediment cap of surface area A per unit time, F_c would be multiplied by A to give

$$\text{Total contaminant release rate} = F_c A \quad (45)$$

where A is the surface area of the cap [L²] and the units for total contaminant loading are mass per time [M/T].

In those situations where the pore water in the cap is stagnant, v and therefore v_z would be equal to zero, and the first term on the right side of Equations 43 and 44 can be ignored. In addition, the contribution of mechanical mixing ($\alpha_L v_z$) to the hydrodynamic dispersion coefficient in the vertical direction (D_{Lz}) can also be ignored, and the vertical hydrodynamic dispersion coefficient would become equal to the vertical effective diffusion coefficient (D_{ez}). Under these circumstances, Equation 44 reduces to

$$F_c = -n_e \frac{D_{ez}}{R} \left(\frac{dC}{dz} \right) \quad (46)$$

For nonsorbing contaminants, R is equal to 1 and Equation 41 becomes equal to Equation 9.

$$F_c = -n_e D_{ez} \left(\frac{dC}{dz} \right) \quad (9 \text{ bis})$$

In accordance with Equation 5, as the volume of the medium's solids (V_s) approaches zero, the volume percentage (as a decimal fraction) of the void space in the medium (V_v), and therefore the total porosity (n) and the effective porosity (n_e) approach 1. Diffusion under these assumptions would occur unhindered by the presence of the matrix solids and D_{ez} in Equation 9 (bis) would be replaced by D , the diffusion coefficient for a solute in a liquid. Setting n_e equal to 1, replacing D_{ez} by D , and substituting dl for dz leads to Equation 3 (bis), Fick's first law for diffusion within a free liquid.

$$F = -D \left(\frac{dC}{dl} \right) \quad (3 \text{ bis})$$

3 Transport Models and Cap Performance Predictions

Overview

This chapter discusses the performance of an engineered or naturally deposited sediment cap in the context of 1-D contaminant-transport models. Each of these models conceptually represents the mechanism(s) affecting transport, and includes a governing equation mathematically defining the spatial and temporal interactions among the transport parameters and a solution to the governing equation reflecting initial and boundary conditions appropriate for the prediction of cap performance. In accordance with the discussion in Chapter 2, the use of a vertically oriented 1-D contaminant transport model to predict cap performance is based upon the planar geometry exhibited by most sediment deposits and sediment caps. As before, the 1-D model is assumed to be aligned with the vertically oriented z -axis.

Three distinct 1-D transport models and solutions are presented: the diffusion model, the advection model, and the advection-dispersion model.¹ These models mirror the transport mechanisms previously discussed. The diffusion model is applicable to settings where the Peclet (P_e) number is significantly less than 1 and transport is predominantly driven by the gradient in the dissolved contaminant concentration. In those settings where the P_e number is significantly above 1 and mechanical mixing (mechanical dispersion) can be ignored, transport is primarily driven by energy gradients and dominated by groundwater flow. In such settings, use of the advection transport model is appropriate. In those situations where the effects of groundwater flow, mechanical mixing, and/or diffusion must be considered, use of the advection-dispersion model is required.

The governing equations for the transport models are based upon the law of mass conservation. Mass conservation is incorporated in each of the governing equations through the use of an appropriate equation of continuity in the derivation of the governing equation. Governing equation derivation is based upon the

¹ The solutions to the transport models presented in this report are calculus based. A numerical solution to the 1-D advection-dispersion equation for sediment caps consisting of one or more layers has been developed by the Hazardous Substance Research Centers, South and Southwest, and Louisiana State University. The capping design model can be found at <http://www.hsrc.org/hsrc/html/ssw/> on the Internet.

insertion of a mass flux equation into an appropriate form of the equation of continuity. For the governing equation for the diffusion model that presumes the insignificance of groundwater motion, the mass conserved by the continuity equation is the contaminant mass and the appropriate flux equation is Fick's first law. For the governing equations for advection and the advection-dispersion models, the mass conserved by the equation of continuity and addressed by the flux equation includes both groundwater and contaminant components. In accordance with Chapter 2, the contaminants are assumed to be chemically stable, and the effects of contaminant decay on mass conservation are not addressed in the transport models presented below.

The equations presented in Chapter 2 of the document did not include derivatives with respect to time or spatial derivatives higher than first order. This reflects the fact that the concentration and energy gradients driving transport in Chapter 2 were implicitly treated as constants, which did not vary spatially (specifically in the vertical direction through the sediment cap) and did not depend on time. Although the assumption of a constant energy gradient is retained (more about this below), all of the governing equations for transport presented in Chapter 3 include a first-order derivative of concentration with respect to time ($\partial C/\partial t$). In addition, the governing equations for the diffusion model and the advection-dispersion model include a second-order derivative of concentration with respect to distance ($\partial^2 C/\partial z^2$ or $\partial/\partial z \partial C/\partial z$), while the governing equations for the advection and the advection-dispersion include a first-order concentration derivative with respect to distance ($\partial C/\partial z$).

The presence of the time derivative for concentration in the governing equations indicates that, as transport proceeds, the contaminants will move upward into the cap and the contaminant concentration at any given point in the cap can consequently change. In the case of the diffusion and advection-dispersion models, the presence of the second-order concentration derivative in the governing equations indicates that the slope in the spatial distribution of contaminant concentrations along the sigmoidally shaped contaminant front changes with location. Inclusion of both the first-order time and second-order spatial derivative in the diffusion and advection dispersion governing equations reflects the evolution in the length and shape of the initially abrupt contaminant front during transport. This should come as no surprise given the discussions presented in Chapter 2 regarding the development of the contaminant front during transport due to diffusion and mechanical mixing. The advection model, in contrast, ignores the spreading along the contaminant front due to these factors and does not include a second-order spatial derivative. The first-order spatial derivative for concentration in both the advection and advection-dispersion governing equations allows for the vertical migration of the center of the contaminant front into and through the cap due to the vertical flow of groundwater at velocity v_z .

The governing equations for both the advection and the advection-dispersion models include the magnitude of the vertical component of the groundwater velocity (v_z) as a constant coefficient. This implicitly presumes that the groundwater flow regime in the vicinity of the cap is uniform and steady-state. Steady-state groundwater flow occurs when the direction and magnitude of flow throughout the sediment cap does not change with time, while uniformity

presumes that the magnitude of v_z does not change with position. Therefore, in accordance with Equation 16, steady-state uniform groundwater flow throughout the cap also assumes that the vertical energy or hydraulic gradient (dh/dz) does not change with time or position. Similarly, the absence of v_z from the governing equation in the diffusion model is consistent with the view that use of the diffusion model presumes that the hydraulic gradient and therefore v_z equal zero, i.e., that the groundwater within the cap is stagnant. In addition to v_z , the governing equations for the transport models in this section also include constant coefficients values for R , D_{ez} , and D_{Lz} , which are similarly assumed not to change with time or position.

As provided in the discussion that follows, the solutions to each of the three sediment cap performance models can be modified to address the effects of contaminant retardation due to sorption. As noted, retardation can significantly slow the passage of contaminants through the cap and is an important factor in cap performance.

One-Dimensional Transport Models and Sediment Caps

Using a 1-D model to describe contaminant transport through a sediment cap entails solving an appropriate differential equation for the spatial interval of interest. The differential equation is the governing equation and the limits of the interval of interest are termed boundaries. Solving the governing equation requires information regarding the initial conditions within the interval, and both the initial state and any changes through time on the interval boundaries. Together, the governing equation and statements regarding the initial and boundary conditions constitute a class of differential equations called initial, boundary-value problems. Solution of the 1-D governing equation for the associated initial and boundary conditions establishes the behavior within the interval enclosed by the boundaries through time.

For capping and natural recovery problems, the interval of interest is a line of length \mathcal{L} , aligned along the vertically oriented z -axis, extending upward from the base to the top of the cap, where \mathcal{L} is the cap thickness. The behavior of interest is the dissolved contaminant concentrations along this vertical interval \mathcal{L} over time. The change in contaminant concentrations along this interval is presumed to represent the migration of the contaminants over time and therefore the behavior of the cap as a whole.

Characteristics of the cap boundaries are defined by the aqueous contaminant concentration in the pore water at the base of the cap (the source concentration, C_o) and the aqueous contaminant concentration in the pore water at the top of the cap (the cap/surface-water interface). At most sites, the contaminant concentration in the overlying surface water will be very low relative to C_o . For simplicity, this concentration will be assumed to equal zero. Similarly (as before), the initial contaminant concentration in the pore water of the sediment cover layer will also be assumed to be zero and consequently equal to the contaminant concentration

in the overlying surface-water body. Throughout the transport process, C_o is maintained at a constant level by the dissolution of the contaminants sorbed to the sediment layer solids.

Location of the top of the cap is determined by the thickness of the cap \mathcal{L} , which mathematically as a boundary can be handled in several ways. One approach is based upon the assumption that the cap is infinitely thick and extends from the base of the cap vertically to infinity. Accordingly, a solution to the governing equation based upon this approach is referred to as a semi-infinite solution. Despite being physically unrealistic, the semi-infinite assumption can provide a viable solution if contaminant transport rates are not significantly affected by the limited thickness of the cap and the close proximity of the low contaminant concentrations in the overlying surface water. Under the semi-infinite scenario, contaminant concentrations and breakthrough times for the cap surface are solved at a distance down-gradient of the source corresponding to the thickness of the cap at \mathcal{L} .

A second method for dealing with the down-gradient boundary provides a solution to the governing equation, which accounts for the limited thickness of sediment caps in the real world. Accordingly, these solutions are referred to as finite-domain solutions. Although more accurate, the finite-domain solutions are more involved mathematically. The added complexities are needed to address the presence of the low contaminant concentrations in the overlying surface water at a distance from the source (the sediment layer) equal to the cap thickness \mathcal{L} .

Although the thicknesses of real-world sediment caps must obviously be finite, and despite the enhanced accuracy provided by the finite-domain solutions, the simpler semi-infinite solutions are commonly used to predict the performance of sediment cover layers (USEPA 1998, Appendix B). This is the approach that will be followed in this report, where only the semi-infinite solutions are provided. In general, the semi-infinite solutions will better approximate the finite-domain solutions for short transport times into relatively thick caps, where the contaminant front is at some distance from the cap's upper boundary and when advection dominates transport ($P_e > 1$). Using the advection-dispersion equation to model cap performance, Reible (USEPA 1998, Appendix B) found the semi-infinite and finite-domain solutions to be "essentially identical" for $P_e > 1$, but found the semi-infinite solution underpredicted transport in situations dominated by diffusion ($P_e < 1$). A discussion and comparison of the finite-domain and the semi-infinite solutions to the 1-D advection-dispersion equation can be found in U.S. Department of Agriculture (1982). For further details regarding the various initial and boundary conditions that can be applied to transport simulations in hydrogeologic settings, see Fetter (1993) and the USGS (1992).

The Diffusion Transport Model

As discussed, as the groundwater velocity approaches zero (a P_e value significantly less than 1), conditions become hydrostatic and contaminant transport is dominated by diffusion. In the absence of groundwater flow, diffusion is

the only mechanism by which contaminants are transported from the sediment layer to the overlying body of surface water. Vertical transport by diffusion through the cap is driven by differences in dissolved contaminant concentration between the pore water in the sediment layer and the pore water in the subsequent cap and/or the overlying surface water body.

Conceptually, starting from a horizontal plane over which the contaminant concentration abruptly changes from the source concentration to zero, the contaminant front will over time move vertically upward into the cap. As time advances, the abrupt change in the contaminant concentration across the contaminant front will gradually moderate and lengthen into an interval (Figure 7). The reader should note that the spreading of the contaminant front with time, described above, is the result of diffusion alone, as mechanical mixing is not a factor in the absence of groundwater flow.

Fick's first law (Equation 9) quantifies the vertical rate of contaminant transport through the cap and can be applied to either steady-state scenarios, where the concentration gradient and therefore the diffusive flux are not changing with time, or at any given point in time during a transient (time-dependent) event. Transient events, as noted, would include the evolution of the contaminant front during the diffusive transport of solutes into the cap with time. In settings where the distribution of contaminant concentrations is changing with time, Fick's second law is applicable. For the 1-D transport of a contaminant subject to retardation, Fick's second law can be stated as

$$\frac{\partial C}{\partial t} = \frac{D_{ez}}{R} \left(\frac{\partial^2 C}{\partial z^2} \right) \quad (47)$$

where

$\partial C / \partial t$ = change in contaminant concentration with time [(M/L³)/T]

$\partial^2 C / \partial z^2$ = rate of change of concentration gradient ($\partial C / \partial x$) with vertical distance, i.e., $(\partial / \partial x)(\partial C / \partial x)$ [(M/L³)/L²]

D_{ez} = vertical effective diffusion coefficient [L²/T]

z = vertical distance from the contaminant source [L]

t = time [T]

R = contaminant retardation coefficient [dimensionless]

In the absence of retardation ($R = 1$), Equation 47 reduces to

$$\frac{\partial C}{\partial t} = D_{ez} \left(\frac{\partial^2 C}{\partial z^2} \right) \quad (48)$$

Equations 47 and 48 can be derived from considerations of contaminant mass conservation into and out of a defined portion of the cap volume. This volume is assumed to be vertically oriented (hence, the use of D_{ez} and z) and large enough

to provide a representative average of the pertinent transport characteristics of the cap. Such a volume will be referred to in this report as a representative elementary volume (REV) (Figure 15).

The derivative $\partial C/\partial t$ describes the rate of change with time of the contaminant concentration within the REV. When $\partial C/\partial t$ equals zero, the contaminant concentration within the REV is not changing with time. The term $D_{ez} \partial^2 C/\partial z^2$ (or $D_{ez}/R \partial^2 C/\partial z^2$ in Equation 47) describes the contaminant flux into and out of the REV due to diffusion. When the contaminant mass moving into the REV equals the mass moving out of the REV, $\partial C/\partial t$ equals zero and Fick's second law (Equations 47 and 48) reduces to Fick's first law.

Use of the more complicated second law is needed to describe the changes in the concentration gradient, and the shape of the contaminant front within the cap over time. A derivation of the governing equation for the diffusion model (Fick's second law) can be found in Crank (1964). A discussion of the subtleties associated with the REV concept is provided in Bear and Verruijt (1987).

Boundary and initial conditions

Boundary and initial conditions applicable to Equations 47 and 48 for transport from a planar contaminant source (the layer of contaminated sediments) vertically into an overlying saturated porous medium (the cap) can be stated as

$$C(0,t) = C_o; \quad C(z,0) = 0 \quad \text{and} \quad C(\infty,t) = 0 \quad (49)$$

The first statement [$C(0,t) = C_o$] is a boundary condition applicable to the base of the cap or the sediment/cap interface, and states that the sediment layer acts as a continuous source through time of dissolved contaminants with a concentration equal to C_o (the source concentration). The second statement [$C(z,0) = 0$] is an initial condition, stating that the contaminant concentration throughout the pore space of the cap is zero prior to the initiation of diffusional transport. As such, the position parameter z in Equation 49 represents any position z units of distance above the base of the cap. The third statement [$C(\infty,t) = 0$] stipulates that the cap is infinitely thick (the semi-infinite boundary condition) and that dissolved contaminant concentration at the far end of an infinitely thick cap will never rise above zero. A contaminant concentration of zero at infinity is intuitively reasonable, as transport at a finite rate will never move the contaminant front an infinite distance in a finite period of time. Under the semi-infinite scenario, contaminant concentrations and breakthrough times for the cover surface are solved at a distance down-gradient of the source that corresponds to the top of the sediment cover layer at \mathcal{L} .

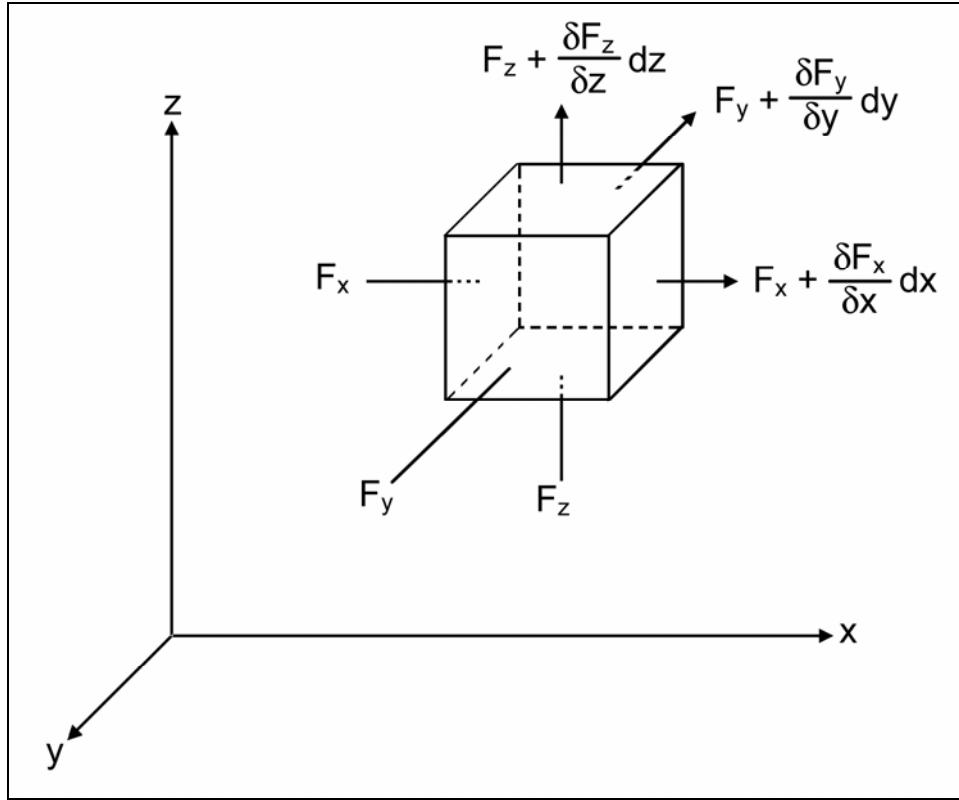


Figure 15. Contaminant Flux Into and Out of an REV: For a vertically oriented 1-D analysis, transport in the x (F_{cx}) and y (F_{cy}) directions is ignored. F_{cz} represents the vertical contaminant flux and depends upon the process being represented. For diffusion, $F_{cz} = -D_{ez}n_e dC/dz$ (Equation 9). For advection, $F_{cz} = v_z n_e C_o$ (Equation 18). For advection and hydrodynamic dispersion, $F_{cz} = v_z n_e C - D_{Lz} n_e dC/dz$ (Equation 43). As this report considers 1-D transport only, F_{cz} is represented as F_c (from Freeze and Cherry 1979)

Solutions applicable to sediment caps

The solution to Equation 47 for a position within the cap a vertical distance z units above the base of the cap, for the boundary and initial conditions provided, is given by

$$\frac{C(z,t)}{C_o} = \text{erfc} \left[\frac{Rz}{2\sqrt{RD_{ez}t}} \right] \quad (50)$$

where

$$\frac{C(z,t)}{C_o} = \text{contaminant concentration normalized to the source concentration [dimensionless]}$$

$$C = \text{dissolved contaminant concentration at position } z \text{ [M/L}^3\text{]}$$

- C_o = sediment layer source concentration [M/L³]
 $erfc$ = complementary error function [dimensionless]
 z = vertical distance above the base of the cap [L]
 t = time since diffusion began [T]
 R = contaminant retardation coefficient [dimensionless]
 D_{ez} = vertical effective diffusion coefficient [L²/T]

As the location of the cap/surface-water interface, performance of the cap can be defined in terms of the dissolved contaminant concentrations at \mathcal{L} . Equation 50 written in terms of \mathcal{L} produces

$$\frac{C(\mathcal{L},t)}{C_o} = erfc \left[\frac{R\mathcal{L}}{2\sqrt{RD_{ez}t}} \right] \quad (51)$$

Nonsorbing contaminants will have an R value equal to 1, while contaminants that sorb to the matrix solids of the cap will have a value of R exceeding 1. Inserting a value of $R = 1$ into Equations 50 and 51 produces (Fetter 1993)

$$\frac{C(z,t)}{C_o} = erfc \left[\frac{z}{2\sqrt{(D_{ez}t)}} \right] \quad (52)$$

$$\frac{C(\mathcal{L},t)}{C_o} = erfc \left[\frac{\mathcal{L}}{2\sqrt{(D_{ez}t)}} \right] \quad (53)$$

Solution interpretation

The solution equations provided above for the diffusional transport model allow the contaminant concentration at any elevation (z) within or at the top of the cap (\mathcal{L}) to be predicted as a fraction of the source concentration (C_o) through time. As diffusion proceeds, the contaminant concentration will gradually increase from the background concentration (zero) and approach C_o with the passage of the contaminant front. Increases in the contaminant concentration with time at a specific location (i.e., a contaminant breakthrough curve at z or \mathcal{L}), or the spatial distribution of contaminant concentrations along the contaminant front at a specific point in time (i.e., a contaminant spatial distribution curve), are presumed to follow a sigmoidal distribution related to the Gaussian (normal) distribution. As noted, the sigmoidal contaminant distribution along the contaminant front can be developed from an approach that results in a cumulative summation of the area beneath a related Gaussian distribution curve. Assuming the contaminant is stable and a background concentration of zero, the contaminant distribution will be centered upon $C_o/2$, the average contaminant concentration along the contaminant front. Dissolved contaminant concentrations less than $C_o/2$ will

precede the center of the front, and concentrations less than $C_o/2$ will follow. The sigmoidal contaminant distribution along the contaminant front is reflected by the presence of the *erfc* in the solutions (Equations 50 through 53) provided above.

The complementary error function (*erfc*) is equal to $1 - \text{erf}$, where *erf* is the error function. The *erf* is the integral of the Gaussian distribution and represents a summation of the area beneath the Gaussian curve. The *erf* and *erfc* values for arguments ranging from zero to positive 3 are provided in Table 1. These tables can also be found in standard hydrogeologic references such as Fetter (1993) and Freeze and Cherry (1979). Although not provided in Table 1, *erfc* values range between 0 and plus 2 (Fetter 1999).

Table 1^{1,2} Values of the Error Function of x[erf(x)] and the Complementary Error Function of x[erfc(x)]					
x	erf(x)	erfc(x)	x	erf(x)	erfc(x)
0	0	1.0	1.1	0.880205	0.119795
0.5	0.056372	0.943628	1.2	0.910314	0.089686
0.10	0.112463	0.887537	1.3	0.934008	0.065992
0.15	0.167996	0.832004	1.4	0.952285	0.047715
0.20	0.222703	0.777297	1.5	0.966105	0.033895
0.25	0.276326	0.723674	1.6	0.976348	0.023652
0.30	0.328627	0.671373	1.7	0.983790	0.016210
0.35	0.379382	0.620618	1.8	0.989091	0.010909
0.40	0.428392	0.571608	1.9	0.992790	0.007210
0.45	0.475482	0.524518	2.0	0.995322	0.004678
0.50	0.520500	0.479500	2.1	0.997021	0.002979
0.55	0.563323	0.436677	2.2	0.998137	0.001863
0.60	0.603856	0.396144	2.3	0.998857	0.001143
0.65	0.642029	0.357971	2.4	0.999311	0.000689
0.70	0.677801	0.322199	2.5	0.999593	0.000407
0.75	0.711156	0.288844	2.6	0.999764	0.000236
0.80	0.742101	0.257899	2.7	0.999866	0.000134
0.85	0.770668	0.229332	2.8	0.999925	0.000075
0.90	0.796908	0.203092	2.9	0.999959	0.000041
0.95	0.820891	0.179109	3.0	0.999978	0.000022
1.00	0.842701	0.157299			
¹ Table 1 does not include values for the <i>erfc</i> when the argument is negative. To determine the value of <i>erfc</i> when the argument is less than 0, the equation $\text{erfc}(-B) = 1 + \text{erf}(B)$ can be used (Fetter 1999).					
² For arguments of <i>erfc</i> approaching zero, <i>erfc</i> is approximately 1. For arguments of <i>erfc</i> equal or exceeding 3, <i>erfc</i> can be approximated as zero.					

In Equation 53, the top of the cap is specified by \mathcal{L} , while $2\sqrt{D_{ez}t}$ is a measure of the width of the contaminant front. The argument of the complementary error function (the ratio of \mathcal{L} to $2\sqrt{D_{ez}t}$) determines the spatial relation of the location of the contaminant front to the top of the cap at \mathcal{L} at any time t . Both the numerator [\mathcal{L}] and the denominator $2\sqrt{D_{ez}t}$ are measured in terms of length [L], making the argument of the *erfc* dimensionless. As noted, with the passage of time the width of the contaminant front will lengthen. In all of the solution equations provided, this is reflected by the product of D_{ez} (a constant) with ever-increasing values of t as the time available for transport increases. When \mathcal{L} is significantly larger than $2\sqrt{D_{ez}t}$,

the argument of $erfc$ is large and the value of the $erfc$ is approximately zero. Physically, this means that the contaminant front is still within the cap and sufficiently distant from \mathcal{L} for the contaminant concentration at the top of the cap to be essentially zero. In contrast, when \mathcal{L} is small relative to $2\sqrt{D_{ez}t}$, the argument of $erfc$ approaches zero and the value of $erfc$ is approximately one. Physically, this means that the contaminant front has moved through the cap and the contaminant concentrations at \mathcal{L} are approximately equal to the source concentration (C_o). In accordance with Equation 52, if predictions of the contaminant concentration over time are desired at another elevation z within the cap, the distance value for z as measured from the base of the cap should be used in place of \mathcal{L} (Figure 16).

For sorbing contaminants, Equation 50 and 51 should be used. These equations include the dimensionless retardation coefficient (R). The presence of R in these equations will cause the contaminant front for sorbing contaminants to be narrower and lag behind the front of nonsorbing contaminants (Figure 14).

The Advection Transport Model

Groundwater discharge to a surface-water body can carry contaminants from the contaminated sediment layer upward through the cap to the cap/surface-water interface and ultimately to the overlying body of surface water. Application of the advection transport model is useful when transport by advection dominates transport by diffusion, i.e., when the Peclet number (P_e) is larger than 1, and when the effects of hydrodynamic dispersion can be ignored. The effects of hydrodynamic dispersion can be ignored when the widening of the contaminant front due to mechanical mixing and diffusion is limited relative to the advective transport distance (v times the transport time, t). For a sediment cap, use of the advection transport model is appropriate if the width of the contaminant front due to hydrodynamic dispersion is at all times prior to contaminant breakthrough a small fraction of the cap's thickness.

Ignoring the effects of diffusion and mechanical mixing, contaminant concentrations in the pore water at any location z units above the base of the cap will change abruptly from the background concentration to the source concentration (C_o) with the passage of the contaminant front. As noted, transport under such conditions is termed plug flow. Plug flow assumes that the passage of the advective contaminant front is associated with a complete replacement of all of the pore water in the cap at that location and that the width of the contaminant front remains essentially zero throughout the transport process. Application of the advection transport model consequently yields a single estimate for the arrival of the contaminant front with a concentration equal to C_o . Unlike the solution to the diffusion transport model, predictions in terms of $0.05C_o$, $0.50C_o$, $0.95C_o$, etc., play no part in the advection transport model.

The governing equation for advective transport can be derived from considerations of mass conservation (Zheng and Bennett 1995). The 1-D governing

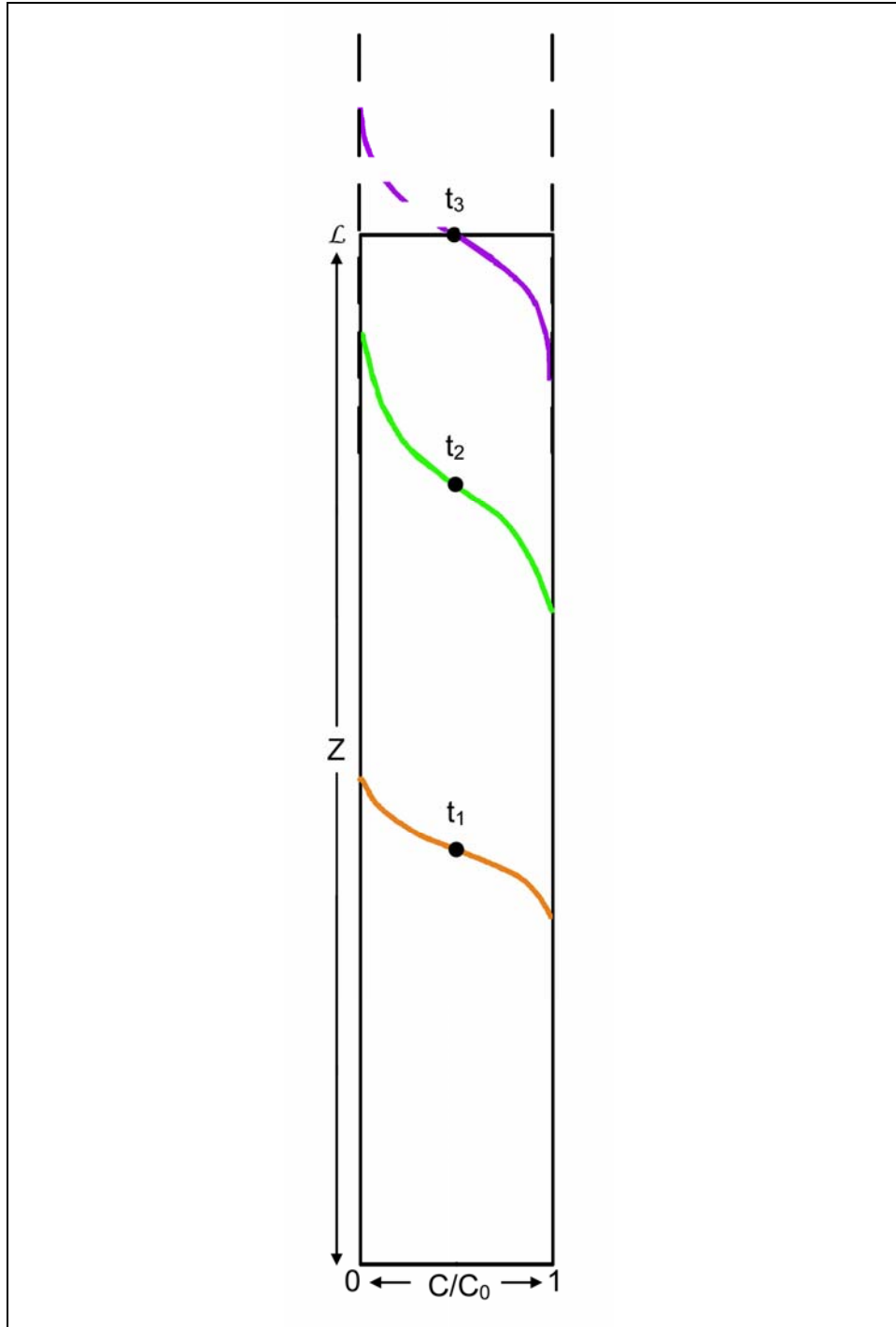


Figure 16. Solution to the Diffusion Transport Model: Starting at time t_0 , the contaminant front will move upward into the cap and moderate into an interval. At times t_1 and t_2 , the contaminant front is well below the top of the cap at L and the arguments of the *erfc* in Equations 51 and 53 are large, resulting in a C/C_0 ratio of approximately zero. At t_3 , the argument of *erfc* and the C/C_0 ratio are approximately 0.5

equation for the advective transport of a sorbing contaminant through a homogeneous, porous cap is (Domenico and Schwartz 1990)

$$\text{Error! Objects cannot be created from editing field codes.} \quad (54)$$

where

$\partial C/\partial t$ = change in contaminant concentration with time $[(M/L^3)/T]$

v_z = vertical component of the advective velocity vector $[L/T]$

R = contaminant retardation coefficient [dimensionless]

$\partial C/\partial z$ = vertical concentration gradient $[(M/L^3)/L]$

As with diffusion, sorption will delay the arrival of the contaminant front at the top of the cap. This behavior will be reflected by a value of the contaminant retardation coefficient (R) greater than one. In the absence of retardation ($R = 1$), the governing equation for advective transport reduces to (Fetter 1993)

$$\frac{\partial C}{\partial t} = -v_v \left(\frac{\partial C}{\partial z} \right) \quad (55)$$

In the governing Equations 54 and 55, the term $\partial C/\partial t$ describes the change in contaminant concentration within a vertically oriented REV with time, while the second term on the right ($v_z/R \partial C/\partial z$ or $v_z/R \partial C/\partial z$) describes the contaminant flux into and out of the REV due to a vertical component of advection or groundwater flow (Figure 15). The fact that the shape of the contaminant front does not evolve as transport proceeds, but remains a horizontal plane over which the contaminant concentrations abruptly changes from the source to the background concentration, precludes the need for a second-order spatial derivative in the governing equation of the advective model. The presence of v_z as a constant coefficient presumes steady-state groundwater flow.

Initial condition

The initial condition applicable to Equations 54 and 55 for groundwater flow from a planar contaminated sediment layer (the contaminant source) into the overlying sediment cover layer (the cap) is

$$C(z,0) = 0 \quad (56)$$

Equation 56 represents the fact that at the start of the advective transport process ($t = 0$), the contaminant concentration in the pore water at all locations within the overlying cap is assumed to equal the background concentration (again usually zero). Because of the reduced order of the governing equation for advection (no second-order derivative), boundary conditions are not required to provide a solution to the governing equation for advection.

Solutions applicable to sediment caps

Using initial condition provided by Equation 56, the solution to the advective transport equation (Equation 54) for a contaminant interacting with the cap solids through sorption and associated with the retardation coefficient equal to R would be

$$v_{zc} = \frac{v_z}{R} = \frac{q_z}{n_e R} = -\frac{K_z}{n_e R} \left(\frac{dh}{dz} \right) \quad (57)$$

where

v_{zc} = vertical component of the linear velocity for a retarded contaminant [L/T]

v_z = vertical component of the linear velocity of groundwater [L/T]

q_z = vertical component of the average specific discharge through the cap [L/T]

n_e = effective porosity [dimensionless]

K_z = vertical hydraulic conductivity [L/T]

dh/dz = vertical component of the hydraulic gradient through the cap [dimensionless]

In the absence of retardation ($R = 1$), the velocity of the contaminant vertically through the cap will equal the vertical component of the advective or groundwater velocity vector, and v_{zc} will equal v_z . Thus, Equation 57 becomes

$$v_{zc} = v_z = \frac{q_z}{n_e} = -\frac{K_z}{n_e} \left(\frac{dh}{dz} \right) \quad (58)$$

Solution interpretation

Equations 57 and 58 are 1-D versions of Darcy's law (Equations 14 through 16), which describe the rate of movement of an advectively driven contaminant front vertically through the cap. Specifically, Equation 57 provides an estimation of the vertical component of the average linear velocity for contaminants with a retardation coefficient value greater than 1, while Equation 58 provides an estimation of the vertical component of the average linear velocity for both groundwater and nonsorbing contaminants. Under ideal conditions, the advective transport model predicts that the advective contaminant front will move uniformly upward through the sediment cover layer as a horizontal plane with a contaminant concentration equal to the source concentration (C_o) (Figure 13).

As discussed previously, a performance criterion of significance for capping and natural recovery projects is the breakthrough time (T_B). This represents the amount of time the contaminant front resides within the sediment cover layer. Breakthrough time is a function of the contaminant's vertical advective velocity

$(v_z/R$ or $v_{zc})$ and the thickness of the cap $[\mathcal{L}]$. At any time prior to breakthrough, the location of the contaminant front within the cap is z or $v_{zc} t$, where t is the time of transport.

Time required for breakthrough (T_B) through a sediment cap of thickness \mathcal{L} for a contaminant with a retardation coefficient equal to R would be

$$T_B = \frac{\mathcal{L}}{v_{zc}} = \mathcal{L} \frac{R}{v_z} \quad (59)$$

where v_{zc} is the vertical advective velocity of the retarded contaminant.

As indicated by Equation 59, the breakthrough time for a sorbing contaminant is directly proportional to the magnitude of the retardation coefficient R and therefore the contaminant's sorptive tendencies.

For contaminants that are not sorbed, R would equal 1, the contaminant would move through the cap at the rate of the advecting groundwater (v_v) and the breakthrough time (T_B) would be expressed by Equation 17:

$$\text{Advective travel time} = \frac{\mathcal{L}}{v_z} \quad (17 \text{ bis})$$

The Advection-Dispersion Model

The governing equation for the Advection-Dispersion Model considers the transport contribution of both groundwater flow and hydrodynamic dispersion to the migration of contaminants through the sediment cover layer and is called the advection dispersion equation (ADE). As a result, solutions to the ADE include terms representing advection and hydrodynamic dispersion, and are more complicated than the solutions to the two models previously discussed. These solutions provide predictions for the contaminant concentration at any point within the cap (z) or at the top of the cap (\mathcal{L}) through time as a fraction of the source concentration C_o .

In groundwater discharge areas, advection will cause the contaminant front to move upward into and through the cap, while hydrodynamic dispersion will cause the contaminant front to widen as the transport processes proceed. As was assumed for the other models, at the start of the contaminant transport process, the dissolved contaminant concentration throughout the sediment cover is zero and the contaminant front initially starts its migration into the cap as a horizontal plane located at the base of the cap. Across this horizontal plane, contaminant concentration abruptly changes from the source concentration (C_o) to zero. When the contaminant transport process begins (at $t = 0$), dissolved contaminants start their migration into the saturated pore space of the sediment cover layer. The velocity of the contaminant front into the cap is equal to the vertical component of the contaminant's average linear velocity (v_z/R or v_{zc}). Therefore, at any time t ,

the location of the center of the contaminant front within the cap will be equal to the product $v_{zc} t$. Assuming a background concentration of zero and contaminant stability, the center of the contaminant front will be associated with a contaminant concentration equal to $C_0/2$, the average contaminant concentration along the contaminant front.

As transport progresses, processes associated with hydrodynamic dispersion will cause the initially abrupt contaminant front to widen. Like the solution for the diffusion transport model, the distribution of contaminant concentrations across the contaminant front follows a distribution related to the Gaussian/normal distribution (Fetter 1993). This is denoted by the presence of the complementary error function (*erfc*) in the solution to the ADE, which reflects the fact that the distribution of contaminant concentrations along the contaminant front is sigmoidal and ranges from the background concentration (zero) to C_0 . Once the contaminant front has passed completely through the cap, the contaminant concentrations within the cap are everywhere equal to the source concentration (C_0).

The ADE can be derived by relating the mass of the contaminant migrating into and out of a vertically oriented REV to the mass accumulation or loss within the REV (Freeze and Cherry 1979) (Figure 15). The 1-D ADE and the initial and boundary conditions appropriate for sediment caps provide a solution that allows the vertical movement of a contaminant front through the cap to be predicted through time. This transport prediction represents the combined effects of both advection and hydrodynamic dispersion. The 1-D ADE describing the vertical transport of dissolved contaminants through a sediment cap consisting of a saturated porous medium capable of sorbing the migrating contaminants is (Domenico and Schwartz 1990)

$$\frac{\partial C}{\partial t} = \frac{D_{LZ}}{R} \left(\frac{\partial^2 C}{\partial z^2} \right) - \frac{v_z}{R} \left(\frac{\partial C}{\partial z} \right) \quad (60)$$

where

$D_{LZ}/R \partial^2 C/\partial z^2$ = vertical transport due to mechanical dispersion and diffusion [(M/L³)/T]

$v_z/R \partial C/\partial z$ = vertical transport due to advection [(M/L³)/T]

$\partial C/\partial t$ = concentration change with time [(M/L³)/T]

D_{LZ} = vertical hydrodynamic dispersion coefficient [L²/T]

R = contaminant retardation coefficient [dimensionless]

v_z = vertical component of the average advective velocity vector [L/T]

For a nonsorbing contaminant, R is equal to 1, and Equation 60 becomes

$$\frac{\partial C}{\partial t} = D_{LZ} \left(\frac{\partial^2 C}{\partial z^2} \right) - v_z \left(\frac{\partial C}{\partial z} \right) \quad (61)$$

As before, $\partial C/\partial t$ describes the rate of change in the contaminant concentrations in the REV. The terms $v_z/R \partial C/\partial z$ and $v_z \partial C/\partial z$ describe the migration of the contaminant front and the contaminant flux into and out of the REV due to advection. The terms $D_{LZ}/R \partial^2 C/\partial z^2$ and $D_{LZ} \partial^2 C/\partial z^2$ describe the contaminant flux into and out of the REV due to hydrodynamic dispersion and the evolution of the contaminant front with time as transport proceeds. Consequently, these terms describe the changes in the width and shape of the contaminant front with time as it moves vertically upward through the subaqueous cap because of the combined effects of diffusion and mechanical mixing. Once again, the presence of v_z as a constant presumes steady-state groundwater flow. Derivations of the governing equation for the advection-dispersion model can be found in Freeze and Cherry (1979) and Fetter (1993).

Boundary and initial conditions

The semi-infinite boundary and initial conditions for the 1-D ADE applicable to contaminant migration from a planar contaminant source (the layer of contaminated sediments) into an overlying saturated porous medium (the sediment cover layer) can be provided in the form (Fetter 1993)

$$C(0,t) = C_o; \quad C(z,0) = 0 \quad \text{and} \quad C(\infty,t) = 0 \quad (62)$$

These boundary and initial conditions were previously discussed and applied to the governing equation for the diffusion transport model (see Equation 49 and the following discussion). As before, these conditions state that the sediment layer is a continuous contaminant source (equal to C_o), the initial contaminant concentration in the cap is zero, and that, at any time t , the contaminant will never travel an infinite distance.

Solutions applicable to sediment caps

The analytical solution of 1-D ADE (Equation 60) for the boundary and initial conditions identified above and acceptable for capping and natural recovery problems for a contaminant with a retardation coefficient equal to R is provided by (Bedient et al. 1999; USEPA 1998, Appendix B)

$$\frac{C(z,t)}{C_o} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{Rz - v_z t}{2\sqrt{RD_{LZ}t}} \right) + \exp \left(\frac{v_z z}{D_{LZ}} \right) \operatorname{erfc} \left(\frac{Rz + v_z t}{2\sqrt{RD_{LZ}t}} \right) \right] \quad (63)$$

where

$$\begin{aligned}
\frac{C(z,t)}{C_o} &= \text{contaminant concentration normalized to the source concentration [dimensionless]} \\
C(z,t) &= \text{contaminant concentration at vertical position } z, \text{ and any time } t \text{ [M/L}^3\text{]} \\
C_o &= \text{source concentration [M/L}^3\text{]} \\
erfc &= \text{complementary error function} \\
z &= \text{vertical distance above the base of the cap [L]} \\
t &= \text{time since mass transport began [T]} \\
v_z &= \text{vertical component of the average linear groundwater velocity vector [L/T]} \\
D_{LZ} &= \text{hydrodynamic dispersion coefficient [L}^2\text{/T]} \\
R &= \text{contaminant retardation coefficient [dimensionless]}
\end{aligned}$$

When the magnitude of D_{LZ} or z or t is large, the second term on the right side of Equation 63 can be ignored (Freeze and Cherry 1979).

For sediment caps, the value for z will not be large, as the largest value of z is \mathcal{L} (the thickness of the cap), which is generally on the order of a meter. The value of D_{LZ} is also generally not large, as the largest values of D_{LZ} occur when advection dominates the transport processes (see Equation 25 and the following discussion). In this case, the magnitude of D_{LZ} is directly proportional to the length of the flow path, which as noted is limited to the thickness of the cap. However, this report considers sediment caps to be physically stable structures, which remain undisturbed over time (i.e., no erosion). In addition, the breakthrough time or the time the contaminant front resides in the cap for viable capping proposals should be on the order of years or more. Given these assumptions, the magnitude of t should be large. Consequently, the second term on the right side of Equation 63 should be small relative to the first term, and therefore insignificant in predicting the performance of most sediment caps. Ignoring the second term, Equation 63 reduces to

$$\frac{C(z,t)}{C_o} = \frac{1}{2} \left[erfc \left(\frac{Rz - v_z t}{2\sqrt{RD_{LZ}t}} \right) \right] \quad (64)$$

For an unsorbed contaminant, R equals 1, and the solution reduces to

$$\frac{C(z,t)}{C_o} = \frac{1}{2} \left[erfc \left(\frac{z - v_z t}{2\sqrt{D_{LZ}t}} \right) \right] \quad (65)$$

These solutions provide a mathematical description of the processes of advection and hydrodynamic dispersion, allowing the contaminant concentration (C) to be predicted as a percentage of the source concentration (C_o), at any location z units above of the base of the cap at any time t . In practice, the location of environmental significance is at the top of the cap, a distance \mathcal{L} from the base of the cap. Replacing \mathcal{L} for z , the solution assumes the form

$$\frac{C(L,t)}{C_0} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{RL - v_z t}{2\sqrt{RD_{LV}t}} \right) \right] \quad (66)$$

Or, in the absence of retardation,

$$\frac{C(L,t)}{C_0} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{L - v_z t}{2\sqrt{D_{LV}t}} \right) \right] \quad (67)$$

Solution interpretation¹

The factors $(z - v_z t)$ and $(L - v_z t)$ in the numerator of Equations 65 and 67 have units of length. These terms identify either a position z units above the base of the cap or the top of the cap at L , relative to the center of the contaminant front at $v_z t$. The center of the front associated with a concentration of $C_o/2$ would move upward through the cap at velocity v_z .

The denominator $2\sqrt{D_{LV}t}$ also has units of length, and reflects the width of the contaminant front due to the spreading effects of hydrodynamic dispersion with increasing time t . For a contaminant front moving vertically through a porous cap, $2\sqrt{D_{LV}t}$ would be the vertical length of the contaminant front in the cap, i.e., the length along which the contaminant concentrations increase from zero to C_o (Domenico and Schwartz 1990).

Because both the numerator and the denominator have units of length, the quotients and therefore the arguments in Equations 64 through 67 of the complementary error function (*erfc*) are dimensionless.² As with diffusion, the presence of the complementary error function in the solution to the advection-dispersion equation reflects the fact that the spatial arrangement in the contaminant concentrations along the contaminant front is sigmoidal in shape and related to the Gaussian distribution.

The factor $(L - v_z t)$ in Equation 67 and contaminant breakthrough. The factor $(L - v_z t)$ in Equation 67 provides three options regarding the position of the contaminant front relative to the top of the cap at L . Specifically, the top of the cap can be on, before, or after the advancing contaminant front, the center of which (where $C/C_o = 0.5$) will move through the cap at the average linear velocity of groundwater in the vertical direction (v_z) in the absence of retardation (Figure 17) (Domenico and Schwartz 1990).

¹ Although specifically addressing the migration of contaminants through a sediment cap, much of the following discussion parallels the presentation provided by Domenico and Schwartz (1990).

² As R is dimensionless, its presence in Equations 64 and 66 does not affect their dimensions.

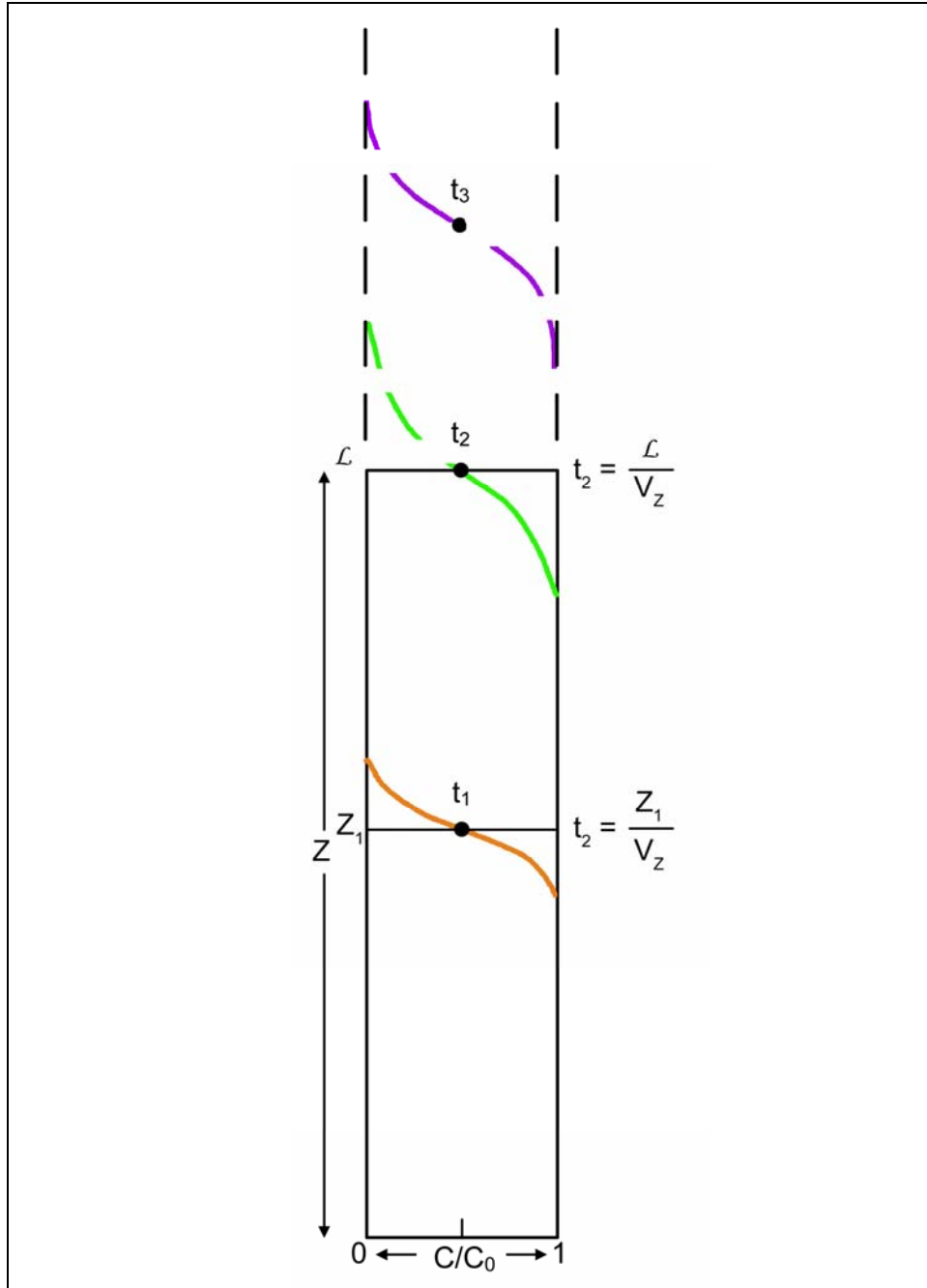


Figure 17. Solution to the Advection-Dispersion Equation: Starting at t_0 , the contaminant front will move into the cap and moderate into an interval. At t_1 , the argument of the erfc in Equations 66 and 67 is large ($R_L > v_v t$ and $L > v_v t$), the C/C_0 ratio is approximately zero, and the contaminant front is well below the top of the cap. At t_2 , the argument of the error function is zero ($R_L = v_v t$ or $L = v_v t$), C/C_0 equals 0.5, and the contaminant front has reached the top of the cap. At t_3 , the argument of the erfc is negative ($R_L < v_v t$ or $L < v_v t$), C/C_0 equals one, and the contaminant front has passed through the cap

- a. \mathcal{L} is before the center of the contaminant front; $C/C_o \ll 0.5$: If the top of the cap at \mathcal{L} is significantly ahead of the advancing contaminant front, the magnitude of \mathcal{L} will be significantly greater than the magnitude of $v_z t$ and the argument of *erfc* is positive. The *erfc* values for positive arguments exceeding 2 are very small, leading to C/C_o ratios approaching zero. In essence, \mathcal{L} is still sufficiently ahead of the advancing contaminant front for the contaminant concentrations at \mathcal{L} to be essentially equal to the background concentration (t_1 in Figure 17).
- b. The center of the contaminant front is at \mathcal{L} ; $C/C_o = 0.5$: When $\mathcal{L} = v_z t$, the argument of the *erfc* equals zero, and the value of the *erfc* equals 1. This leads to the C/C_o ratio of 0.5. This means that the center of the contaminant front has reached the top of the cap (t_2 in Figure 17).
- c. \mathcal{L} is after the center of the contaminant front; $C/C_o \gg 0.5$: When \mathcal{L} is behind the advancing contaminant front, the magnitude of \mathcal{L} is less than $v_z t$ and the argument of *erfc* is negative. As \mathcal{L} is a constant (the cap is stable over time, no erosion) and the magnitude of $v_z t$ is increasing with time, the difference between \mathcal{L} and $v_z t$ becomes more negative with increasing t . When the argument of the *erfc* is approximately -2, the C/C_o ratio is approximately 1 and the contaminant concentrations in the pore water at \mathcal{L} are approximately equal to the source concentration C_o (t_3 in Figure 17). At this point, the contaminant front has moved completely through the cap.

If predictions of the dissolved contaminant concentrations are desired at a location within the cap z units of distance above the base, Equations 64 and 65 should be used. In these equations z replaces \mathcal{L} and the interpretation provided above regarding the concentration changes over time at the top of the cap would now apply to position z .

For sorbing contaminants, Equations 64 and 66 should be used. These equations include the dimensionless retardation coefficient (R). The presence of R will cause the contaminant front for sorbing contaminants to be narrower and lag behind the front of nonsorbing contaminants (Figure 14).

It should also be noted that as v_z approaches zero and conditions become hydrostatic (a P_e value significantly less than 1), D_{LZ} becomes equal to D_{ez} , and the solution to advection-dispersion equation provided by Equation 63 reduces to the solutions provided for the diffusion model by Equations 50 through 53 (Shackelford 1991).

Significance of hydrodynamic dispersion

As noted, $2\sqrt{D_{LZ}t}$ or $2\sqrt{RD_{LZ}t}$ is the vertical length of the contaminant front in the cap, i.e., the vertical length along the contaminant front over which concentrations range from background (zero) to C_o . Because of the presence of t , the length of the contaminant front will lengthen with time. If the width of the

contaminant front at the time of breakthrough (T_B) is notably less than the thickness of the sediment cap, effects of hydrodynamic dispersion can probably be ignored and cap performance can be adequately described by the simpler advection transport model. In contrast, if the width of the contaminant front at the time of breakthrough is significant relative to the cap's thickness, the more complicated advection-dispersion model should be used.

Relationship of the advection-dispersion model to the diffusion and advection models. In the absence of groundwater flow, mechanical mixing is no longer a factor and spreading of the contaminant front with time will depend upon diffusion alone. Consequently, in accordance with Equation 25, when v_z equals zero, D_{LZ} becomes equal to the effective diffusion coefficient, D_{ez} , and the terms $v_z/R \partial C/\partial z$ and $v_z \partial C/\partial z$ drop from Equations 60 and 61. Given conformance with these conditions, the ADE (Equation 60) becomes

$$\frac{\partial C}{\partial t} = \frac{D_{ez}}{R} \left(\frac{\partial^2 C}{\partial z^2} \right) \quad (47 \text{ bis})$$

Equation 47 was presented earlier as Fick's second law for sorbing contaminants. If R equals 1, Equation 60 becomes Fick's second law for nonsorbing contaminants (Equation 48).

$$\frac{\partial C}{\partial t} = D_{ez} \left(\frac{\partial^2 C}{\partial z^2} \right) \quad (48 \text{ bis})$$

If both the mixing effects of diffusion and mechanical dispersion are ignored, the hydrodynamic dispersion coefficient (D_{LZ}) can be set equal to zero, and the terms $D_{LZ}/R \partial^2 C/\partial z^2$ and $D_{LZ} \partial^2 C/\partial z^2$ drop from the governing equations. Given these assumptions, the ADE for sorbing contaminants becomes the 1-D advective-transport equation (Equation 54).

$$\frac{\partial C}{\partial t} = -\frac{v_z}{R} \left(\frac{\partial C}{\partial z} \right) \quad (54 \text{ bis})$$

In the absence of retardation, $R = 1$ and Equation 54 becomes Equation 55, the governing equation for the advection transport model for nonsorbing contaminants.

$$\frac{\partial C}{\partial t} = -v_z \left(\frac{\partial C}{\partial z} \right) \quad (55 \text{ bis})$$

Cap Predictions Versus Cap Performance

This report presented 1-D methods and models that can be used to predict the transport of dissolved contaminants through sediment caps placed either naturally or artificially. Transport predictions can in turn be related to the performance of

the sediment cap, and can be used to project impacts to surface-water quality and biota and to compare the effectiveness of capping and natural recovery to other remedial options such as dredging.

These methods and models use input values describing the characteristics of the sediment cap and its surroundings to generate output values, which estimate the performance of the cap. As discussed, these approaches as well as the input values are subject to a variety of assumptions, including the physical stability of the cap and the uniformity of the cap and its surroundings. In reality, sediment caps can erode and uniformity is seldom realized. Consequently, compliance with the assumptions of the method or model can be limited. Assumption noncompliance or input valuation errors will result in output values that would be misleading indicators of cap performance.

The authors wish to emphasize that the output provided by these methods and models are cap performance predictions. These predictions can be viewed as forecasts as to how the cap should behave if the cap and the surroundings conform with the assumptions inherent in the method or model, and the input values properly reflect the transport characteristics under consideration. In contrast to these projections, the actual performance of the cap as well as conformance with the performance predictions can be determined only through a monitoring program designed to measure the behavior of the cap in the field.

4 Conclusions

Conclusions based on research reported herein are summarized below.

- a. *Cap performance.* The performance of a subaqueous cap is defined in part by its influence on vertical movement of dissolved contaminants. This is reflected in the 1-D analysis approach used in this report where only vertical vector components and parameter values affecting transport upward through the planar cover layer are considered. Cap performance predictions can be defined by the length of time that the contaminant front resides within the cap (breakthrough time), and after breakthrough, the contaminant flux through the cap (contaminant loss rate per unit area per unit time).
- b. *Contaminant decay.* This report has assumed that the source concentration (C_o) is a constant throughout the time interval of interest. This is equivalent to assuming that the contaminant under consideration is stable and that losses due to transport will not significantly reduce the contaminant concentrations in the sediment layer. This in turn is premised upon the fact that groundwater velocities are generally low and that many of the most problematic sediment-bound contaminants are chemically stable, hydrophobic compounds with low solubilities that dissolve slowly in water. Contaminant decay should be assumed to be insignificant unless demonstrated to be otherwise through the analysis of data collected in the field at the site under consideration.
- c. *Groundwater flow or advection.* Groundwater always flows from areas associated with high energy to areas associated with low energy. In the nearshore portions of many surface water bodies, the flow of groundwater will be associated with an upward component. It is the upward-flow component that can move dissolved contaminants through the overlying sediment cap and that affects cap performance. In many settings, the performance of the cap will be largely controlled by the presence or absence of groundwater flow. Given the fine-grained nature of most contaminated sediment deposits, and cap thicknesses on the order of a meter, placement of a cap consisting of sand-sized particles should not significantly alter the groundwater flow regime at the site.
- d. *Hydrodynamic dispersion.* Hydrodynamic dispersion consists of the combined effects of diffusion and mechanical mixing. In 1-D,

hydrodynamic dispersion results in the spreading of the contaminant concentrations in the direction of transport. In settings where the groundwater is in motion, hydrodynamic dispersion will generally be dominated by the effects of mechanical mixing, which in turn is proportional to the magnitude of the advective velocity and the length of the flow path. Because cap thicknesses are limited and flow paths within the cap are short, the effects of mechanical mixing should also be limited. In settings where groundwater flow is minimal, hydrodynamic dispersion is dominated by the effects of diffusion.

- e. *Hydrogeologic site characteristics.* Hydrogeologic characteristics of a proposed capping or natural recovery site are of critical importance to the effectiveness of the sediment cover layer in isolating the contaminants associated with the sediments from the overlying surface water and biota. Site characterization data are needed to identify the transport processes operating at the site and to provide input values for the appropriate transport equations.
- f. *Molecular diffusion.* Molecular diffusion always occurs in the presence of a concentration gradient. In the absence of advection, the transport of contaminants through the cap will be dominated by molecular diffusion, an extremely slow process. Generally, diffusion becomes the dominant transport mechanism in settings associated with very low hydraulic conductivity values and/or where hydrostatic conditions prevail.
- g. *Sediment cap monitoring.* The methods and models presented in this report provide cap performance predictions only and are subject to a variety of assumptions. The actual performance of the cap in the field as well as conformance with the performance predictions can be determined only through monitoring.
- h. *Sorption/retardation.* Because of the limited thickness of most sediment caps, contaminant retardation can be a critical mechanism in cap performance. Contaminant sorption can reduce the effectiveness of the processes associated with contaminant transport by orders of magnitude. In most geologic settings, cap performance will be determined by presence and significance of advection and the contaminant-retardation characteristics of the cap.

References

- Appelo, C. A. J., and Postma, D. (1996). *Geochemistry, groundwater, and pollution*. 3rd corrected print, A. A. Balkema Publishers, Netherlands.
- Bear, J., and Verruijt, A. (1987). *Modeling groundwater flow and pollution*. 1st ed., D. Reidel Publishing Company, Dordrecht, The Netherlands.
- Bedient, P. B., Rifai, H. S., and Newell, C. J. (1999). *Ground water contamination; transport and remediation*. 2d ed., Prentice Hall, New Jersey.
- Chapra, S. C. (1997). *Surface water-quality modeling*. McGraw-Hill Companies, Inc., New York.
- Crank, J. (1964). *The mathematics of diffusion*. Clarendon Press, University of Oxford, UK.
- Domenico, P. A., and Schwartz, F. W. (1990). *Physical and chemical hydrogeology*. 1st ed., John Wiley and Sons, New York.
- Faure, G. (1998). *Principles and applications of geochemistry*. 2nd ed., Prentice Hall, New Jersey.
- Fetter, C. W. (1993). *Applied hydrogeology*. 3rd ed., MacMillan, New York.
- _____. (1999). *Contaminant hydrogeology*. 2nd ed., Prentice Hall, New Jersey.
- _____. (2001). *Applied hydrogeology*. 4th ed., Prentice Hall, New Jersey.
- Freeze, R. A., and Cherry, J. A. (1979). *Groundwater*. 1st ed., Prentice Hall, New Jersey.
- Garrels, R. M., and Christ, C. L. (1965). *Solutions, minerals, and equilibria*. Harper and Row, New York.
- Hubbert, M. K. (1940). "The theory of groundwater motion," *The Journal of Geology* XLVIII(8), Part I (Nov/Dec).

- Liu, C., Jay, J., Ika, R., Shine, J., and Ford, T. (2001). "Capping efficiency for metal-contaminated marine sediment under conditions of groundwater discharge," *Environmental Science and Technology* 35(11).
- National Research Council. (2001). "A risk-management strategy for PCB-contaminated sediments, 2001," Committee on Remediation of PCB-Contaminated Sediments, Board on Environmental Studies and Toxicology, Division on Life and Earth Studies, National Academy Press.
- _____. (1997). "Contaminated sediments in ports and waterways, Cleanup strategies and technologies," Committee on Contaminated Marine Sediments, Marine Board, Commission on Engineering and Technical Systems, National Research Council, National Academy Press.
- Rumer, R. R., and Mitchell, J. K., editors. (1995). *Assessment of barrier containment technologies, A comprehensive treatment for environmental remediation applications*. Section 10, "Contaminant transport modeling," by A. J. Rabideau. Prepared for U.S. Department of Energy, U.S. Environmental Protection Agency, DuPont Company. National Technical Information Service, Springfield, VA.
- Shackelford, C. D. (1991). "Laboratory diffusion testing for waste disposal; A review," *Journal of Contaminant Hydrology*, 7, 177-217.
- Suthersan, S. S. (1997). *Remediation engineering: Design concepts*, CRC Lewis Publishers, Boca Raton, FL.
- U.S. Department of Agriculture. (1982). "Analytical solutions of the one-dimensional convection-dispersive solute transport equation," Technical Bulletin 1661, M. Th. van Genuchten and W. J. Alves, authors. Washington, DC.
- U.S. Environmental Protection Agency. (1996a). "Assessment and remediation of contaminated sediments (ARCS) program; Estimating contaminant losses from components of remediation alternatives for contaminated sediments," EPA 905-R96-001, Washington, DC.
- _____. (1996b). Superfund Soil Screening Guidance: Users Guide; Publication 9355.4-23, Part 5, Chemical-Specific Parameters; July 1996.
- _____. (1998). M. R. Palermo, J. Miller, D. D. Reible; Assessment and Remediation of Contaminated Sediments; ARCS, EPA 905-B96-004.
- _____. (1999). Understanding Variation in Partition Coefficient, K_d , Values; EPA 402-R-99-004B, Volumes I and II, August 1999.
- U.S. Geological Survey. (1992). "Analytical solutions for one-, two-, and three-dimensional solute transport in groundwater flow systems with uniform flow," Chapter B7, Applications of Hydraulics, *in* Techniques of Water-Resources Investigations (TWRI) Book 3. E. J. Wexler, author. Reston, VA.

U.S. Geological Survey. (1984). "Computer model of one-dimensional equilibrium-controlled sorption processes," Water-Resources Investigations Report 84-4059. D. B. Grove and K. G. Stollenwerk, authors. Reston, VA.

Winter, T. C. (2002). "Subaqueous capping and natural recovery: Understanding the hydrogeologic setting at contaminated sediment sites," Technical Note ERDC TN-DOER-C26, U.S. Army Engineer Research and Development Center, Vicksburg, MS. <http://libweb.wes.army.mil/uhtbin/hyperion/TN-DOER-C26.pdf>.

Zheng, C., and Bennett, G. D. (1995). *Applied contaminant transport modeling; Theory and practice*. Van Nostrand and Reinhold, New York.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) September 2005		2. REPORT TYPE Final report		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Sediment Capping and Natural Recovery; Contaminant Transport Fundamentals with Applications to Sediment Caps				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) David M. Petrovski, Maureen K. Corcoran, James H. May, and David M. Patrick				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Region 5, U.S. Environmental Protection Agency, 77 W. Jackson Boulevard, Chicago, IL 60604-3511 U.S. Army Engineer Research and Development Center, Geotechnical and Structures Laboratory, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199 The University of Southern Mississippi, 118 College Drive, Hattiesburg, MS 39406-0001				8. PERFORMING ORGANIZATION REPORT NUMBER ERDC/GSL TR-05-19	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL 60604-3511 Headquarters, U.S. Army Corps of Engineers, Washington, DC 20314-1000				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Engineered sediment caps and natural recovery are in situ remedial alternatives for contaminated sediments, which consist of the artificial or natural placement of a layer of material over a sediment deposit, respectively. In addition to physical isolation and the prevention of sediment erosion, the objective of these approaches includes mitigating the loss of dissolved contaminants from the sediment deposit to the overlying surface water. Whether engineered or placed naturally through sedimentation, migration of contaminants through the cover layer needs to be evaluated to forecast performance and compare the effectiveness of capping or natural recovery to other remedial options such as dredging. This report reviews the techniques commonly used to predict the migration of contaminants through sediment cover layers and to assess performance. Predicted upon the planar nature of the sediment deposit and cover layer, these techniques commonly take the form of vertically oriented one-dimensional (1-D) methods and models. These 1-D approaches use input values describing the characteristics of the sediment cap and the hydrogeologic surroundings and generate output values that are used to project cover-layer performance. The assumptions implicit in the use of the 1-D methods and models are also discussed. Much of the information in this report was gathered from standard references in the hydrogeologic literature.					
15. SUBJECT TERMS Contaminant migration Natural recovery			Remedial performance Sediment cap Sediment remediation		
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (include area code)
				84	